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<b>Abstract</b> <p>Reactive distillation has enormous potential for the economical synthesis of tertiary ethers. Methyl tert-butyl ether (MTBE) has been commercially produced with this technology since the early 1980s and it appears that the process also has application for Ethyl tert-butyl ether (ETBE) and other ethers. However, the combination of reaction and distillation in a single unit operation produces a process complexity that inhibits expeditious design and tight control, and presents a technology risk for potential developers. This particularly applies to hybrid reactive distillation where both reactive and non-reactive column sections are employed.</p> <p>The steady state simulation of a series of reactive distillation columns and processes for the production of ETBE and MTBE illuminated a number of important issues related to the optimal design techniques. Many of these issues are peculiar to reactive distillation and would not reasonably be anticipated without a priori knowledge of the phenomena involved. For example, the addition of theoretical equilibrium stages and an increase in the reflux ratio do not always have a directionally equivalent effect. The trade-off between energy consumption and capital cost which is the basis for most distillation designs cannot always be applied to reactive distillation. Importantly, the use of standard modelling techniques for equilibrium processes was also validated for reactive distillation design.</p> <p>The use of residue curve diagrams and reactive residue curve diagrams for the design of reactive distillation processes was investigated and shown to provide useful information regarding the feasibility of reaction-separations. Combined with simulation tools (e.g. Pro/II and SpeedUp), these techniques form the basis of a proposed design strategy for</p>	

hybrid reactive distillation. It is important to apply these design tools appropriately and to select the correct process for a given application. The optimal design must also consider economics and the relative values of products, reactants and energy. These issues were studied with respect to ETBE production for gasoline oxygenation.

The complexity of hybrid reactive distillation not only presents design challenges but potentially makes the process more difficult to control. Dynamic simulations of ETBE and MTBE reactive distillation processes were used to explore some unusual dynamic phenomena and to elucidate the process non-linearity and bidirectionality of reactive distillation. The presence of multiple steady states for some reactive distillation columns has been documented previously but the analysis of this behaviour has been incomplete and somewhat flawed. It was shown that the distinction between molar inputs and physically realisable mass or volumetric inputs is crucial and that multiplicity could be present in one case and not in the other. Multiplicity that is only observed with molar inputs (relatively common) was termed pseudo-multiplicity. Pseudo-multiplicity has few implications for the operation and control of practical reactive distillation processes although most literature examples of multiple steady states fall into this category. Four distinct causes of output multiplicity were identified including one new cause, reaction hysteresis, which is only applicable to hybrid reactive distillation. It was shown, using dynamic simulations, that transitions between parallel steady states are possible for a range of physically realisable and practical disturbances. This contrasts with other work in the area, which examines only unrealisable events and control schemes.

An extensive analysis of reactive distillation control was also undertaken with respect to ETBE and MTBE hybrid columns. Manual (open-loop) control was shown to be impractical due to the need to sustain the operating conditions at close to the optimal values in order to produce acceptable process performance. One-point composition control was found to be relatively easy to implement and effective with either an energy-balance or a material-balance control scheme provided only one steady state was present. Where multiple steady states exist, there are restrictions on the feasible control structures due to unavoidable instability in the inventory controllers. For example, if multiple steady states exist for the one value of the reboiler duty, only the bottoms product draw rate can be used to control the reboiler sump level. Thus, a material-balance control structure that uses the reboiler duty to control the sump level cannot be implemented in practice. Two-point control was also investigated and found to effectively prevent transitions between parallel steady states. Although more complex and difficult to implement than one-point control, a two-point scheme could be used successfully to control both the product composition and the reactant conversion and this could be desirable in some cases.

A reactive distillation pilot plant was designed and operated for ETBE synthesis from ethanol and a locally available refinery hydrocarbon stream. The design of the pilot plant was based on simulation studies and the objective of operating in the industrially significant ranges of product purity and isobutene conversion. A fully automatic control system was designed and installed on the pilot plant to permit precise control of the manipulated variables and the framework to implement a range of control structures and schemes.

Keywords: reactive distillation; process simulation; process design; process control; dynamic simulation; multiplicity; bidirectionality; distillation control; inferential control; pilot plant design and operation.

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**School of Chemical Engineering**

**SIMULATION AND CONTROL  
OF REACTIVE DISTILLATION**

*MARTIN G. SNEESBY, B. ENG. (HONS)*

**This thesis is presented as part of the requirements for the  
award of the Degree of Doctor of Philosophy  
of the  
Curtin University of Technology**

**March, 1998**

## SUMMARY

Reactive distillation has enormous potential for the economical synthesis of tertiary ethers. Methyl *tert*-butyl ether (MTBE) has been commercially produced with this technology since the early 1980s and it appears that the process also has application for Ethyl *tert*-butyl ether (ETBE) and other ethers. However, the combination of reaction and distillation in a single unit operation produces a process complexity that inhibits expeditious design and tight control, and presents a technology risk for potential developers. This particularly applies to hybrid reactive distillation where both reactive and non-reactive column sections are employed.

The steady state simulation of a series of reactive distillation columns and processes for the production of ETBE and MTBE illuminated a number of important issues related to the optimal design techniques. Many of these issues are peculiar to reactive distillation and would not reasonably be anticipated without *a priori* knowledge of the phenomena involved. For example, the addition of theoretical equilibrium stages and an increase in the reflux ratio do not always have a directionally equivalent effect. The trade-off between energy consumption and capital cost which is the basis for most distillation designs cannot always be applied to reactive distillation. Importantly, the use of standard modelling techniques for equilibrium processes was also validated for reactive distillation design.

The use of residue curve diagrams and reactive residue curve diagrams for the design of reactive distillation processes was investigated and shown to provide useful information regarding the feasibility of reaction-separations. Combined with simulation tools (e.g. Pro/II<sup>TM</sup> and SpeedUp<sup>TM</sup>), these techniques form the basis of a proposed design strategy for hybrid reactive distillation. It is important to apply these design tools appropriately and to select the correct process for a given application. The optimal design must also consider economics and the relative values of products, reactants and energy. These issues were studied with respect to ETBE production for gasoline oxygenation.

The complexity of hybrid reactive distillation not only presents design challenges but potentially makes the process more difficult to control. Dynamic simulations of ETBE and MTBE reactive distillation processes were used to explore some unusual dynamic phenomena and to elucidate the process non-linearity and bidirectionality of reactive

distillation. The presence of multiple steady states for some reactive distillation columns has been documented previously but the analysis of this behaviour has been incomplete and somewhat flawed. It was shown that the distinction between molar inputs and physically realisable mass or volumetric inputs is crucial and that multiplicity could be present in one case and not in the other. Multiplicity that is only observed with molar inputs (relatively common) was termed pseudo-multiplicity. Pseudo-multiplicity has few implications for the operation and control of practical reactive distillation processes although most literature examples of multiple steady states fall into this category. Four distinct causes of output multiplicity were identified including one new cause, reaction hysteresis, which is only applicable to hybrid reactive distillation. It was shown, using dynamic simulations, that transitions between parallel steady states are possible for a range of physically realisable and practical disturbances. This contrasts with other work in the area, which examines only unrealisable events and control schemes.

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A reactive distillation pilot plant was designed and operated for ETBE synthesis from ethanol and a locally available refinery hydrocarbon stream. The design of the pilot plant was based on simulation studies and the objective of operating in the industrially significant ranges of product purity and isobutene conversion. A fully automatic control system was designed and installed on the pilot plant to permit precise control of the manipulated variables and the framework to implement a range of control structures and schemes.

**Keywords:** reactive distillation; process simulation; process design; process control; dynamic simulation; multiplicity; bidirectionality; distillation control; inferential control; pilot plant design and operation.

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## BRIEF BIOGRAPHY OF THE AUTHOR

Martin G. Sneesby completed a Bachelor of Engineering degree with first class honours at Curtin University of Technology between 1988 and 1991. As an undergraduate, he received several awards, including the Digby Leach Medal for the Most Promising Graduate from an Engineering Faculty (1991) and the CHEMECA Prize for the Best Chemical Engineering Design Project from an Australian University (1992). He obtained three years of industrial experience with Mobil Adelaide Refinery where he worked as a process engineer and process design engineer, before commencing PhD studies back at Curtin University in 1995 with the assistance of an Australian Postgraduate Award with Stipend (APAWS). Martin is currently employed by Aspen Tech in Cambridge (U.K.) where he builds high fidelity dynamic simulators for operator training and engineering studies. He has written 21 papers and one book on aspects of chemical engineering.

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# NOMENCLATURE

## Abbreviations

AE	Algebraic Equation
DAE	Differential and Algebraic Equation
DIB	Di-isobutene
ETBE	Ethyl tert-Butyl Ether
EtOH	Ethanol
GPDC	Generalised Pressure Drop Correlation
HETP	Height Equivalent to a Theoretical Plate
HTC	Heat Transfer Coefficient
IAE	Integrated Absolute Error
iBut	Isobutene
ITAE	Integrated Time-weighted Absolute Error
LMTD	Log Mean Temperature Difference
MON	Motor Octane Number
MTBE	Methyl tert-Butyl Ether
MeOH	Methanol
MIMO	Multiple Input Multiple Output
MPC	Multi-variable Predictive Control
MSS	Multiple Steady States
NBP	Normal Boiling Point
nBut	n-Butenes
ODE	Ordinary Differential Equation
RGA	Relative Gain Array
RON	Research Octane Number
RVP	Reid Vapour Pressure
SISO	Single Input Single Output
TAME	<i>tert</i> -Amyl Methyl Ether
VLE	Vapour Liquid Equilibrium

## Symbols

$a_i$	Activity of component, i
$A$	Heat transfer area
$B$	Bottoms rate
$D$	Distillate rate <i>or</i> Diameter
$F$	Feed rate
$h$	Liquid height
$H$	Molar enthalpy
$K_A$	Adsorption equilibrium constant
$K_{eq}$	Reaction equilibrium constant
$k_{rate}$	Reaction rate constant
$L$	Molar liquid flow <i>or</i> Reflux rate
$M$	Molar holdup
$m_{cat}$	Mass of catalyst
$P$	Pressure <i>or</i> Profitability
$p^{vap}$	Vapour pressure
$Q$	Heat duty
$R$	Gas constant <i>or</i> Regression coefficient <i>or</i> Electrical resistance
$Re$	Reynold's number
$r_i$	Reaction rate of component, i
$S$	Separation factor
$t$	Time
$T$	Temperature
$U$	Heat transfer coefficient
$V$	Molar vapour flow <i>or</i> Boilup rate <i>or</i> Voltage
$x_i$	Molar liquid concentration of component, i
$X$	Conversion of limiting reactant
$y_i$	Molar vapour concentration of component, i
$z$	Feed composition

## Greek Characters

$\gamma_i$	Activity of component, i
$\lambda$	Relative gain
$\rho$	Density
$\phi$	Phase angle



### **Subscripts and Superscripts**

$0$	Initial condition
$a$	Ambient condition
$C$	Condenser
$L$	Liquid phase
$R$	Reboiler
$V$	Vapour phase

# CHAPTER ONE

## INTRODUCTION

- 1.1 Background**
- 1.2 Motivation and Significance of this Work**
  - 1.2.1 Motivation
  - 1.2.2 Objectives
- 1.3 Thesis Outline**

### 1.1 BACKGROUND

Reactive distillation combines the functionality of a continuous reactor with a conventional distillation column. This fusion of unit operations is not new, it has been in limited use since the 1920s (e.g. methyl acetate production), but a crucial development in the 1980s exposed previously untapped potential and led to a rejuvenation of this technology. The development was the means to support fine catalyst particles in a manner which allows both effective mass transfer and reaction on the surface of the catalyst. This advance permitted heterogeneous reactions to be considered for reactive distillation and introduced the possibility of using hybrid columns which contain both reactive and non-reactive sections. These features have been found to be particularly advantageous for some processes, including the synthesis of methyl *tert*-butyl ether (MTBE).

MTBE is valuable as a gasoline additive which simultaneously increases the octane rating of the fuel and adds oxygen which promotes cleaner burning. When used in place of lead-based octane enhancers, dual environmental benefits are realised: a reduction in atmospheric lead concentrations and reduced emissions of carbon monoxide and other smog forming chemicals. Since the 1970s, the worldwide consumption of MTBE has increased significantly and many new facilities have been constructed to support the growing market (Kirschner, 1996; Riddle, 1996). The success of hybrid reactive distillation in this service has been clearly evident and the technology is now accepted as the best which is currently available.

Ethyl *tert*-butyl ether (ETBE) is an alternative to MTBE which offers a further environmental advantage: the primary raw material, ethanol, can be produced from

renewable resources. ETBE also has superior fuel properties, including a higher octane rating and a low volatility, which enhance its potential. Although MTBE is now widely used, ETBE has remained little more than a novelty and commercial production has been extremely limited. However, a reduction in the cost of ethanol compared with methanol (via subsidies or otherwise) could make ETBE the market leader provided the technological base for commercialisation was available.

The combination of reaction and separation within a single unit operation not only reduces the overall capital cost of a process but provides process benefits in some cases. These benefits arise from the constant recycling of reactants to the reaction zone which increases the conversion of the limiting reactant in an equilibrium limited reaction. A secondary benefit is the increased energy efficiency which results from directly utilising the heat of reaction for fractionation. Reactive distillation is usually justified on steady-state process results but the increased process complexity reduces operability and controllability compared with a conventional two-stage process. Consequently, the full steady-state benefits may not be realisable in dynamic operation, particularly if regular disturbances are likely.

To date, effective, specialised control schemes have not been developed for reactive distillation and a lack of understanding of the process fundamentals has hindered the optimisation of reactive columns. The main source of difficulty in developing an effective control system is the uncertainty of control objectives. It is desirable to simultaneously produce both a high reactant conversion and a high product purity (i.e. it should exactly duplicate both functions of the two-stage process) but the operating conditions which maximise reactant conversion do not necessarily coincide with the conditions which maximise the product purity. Thus, the dual objectives are not entirely compatible.

More recently, reports of multiple steady states in the reactive distillation of MTBE (e.g. Nijhuis et al., 1993; Jacobs and Krishna, 1993) have revealed a further complexity with unique implications for process control. There is a substantial potential for the operation of columns where multiplicity exists to be adversely affected by unwanted transitions between parallel steady states. Output multiplicity has been confirmed at an experimental level in azeotropic distillation (Güttinger et al., 1997), and there appear to be parallels with reactive distillation, but the experimental evidence of multiplicity in reactive distillation has not yet been produced. Several authors have speculated on the physical cause(s) of the simulation-based multiplicities (e.g. Jacobs and Krishna, 1993; Hauan et al., 1995; 1997) and a wide range of explanations has been proposed, but the underlying and fundamental aspects have

not been elaborated and generally only mechanistic descriptions are available. It is clear that this phenomenon is not yet fully understood although there are at least two promising lines of research which appear to offer broadly applicable explanations with strong foundation.

Experimental work on reactive distillation (and particularly hybrid reactive distillation) has been limited to work connected with patent applications and several bench-top studies that focus on the catalyst support mechanism. Although there has undoubtedly been work in the private sector to support process designs, data is not widely available to test modelling techniques and control strategies. There are significant opportunities to make a substantial contribution to the current body of knowledge in each of the areas described above.

## **1.2 MOTIVATION AND SIGNIFICANCE OF THIS WORK**

### **1.2.1 Motivation**

At a fundamental level, this study was motivated by a perceived need to address Australia's worsening urban pollution and smog levels which are caused in a large part by emissions from automotive engines. While our air quality still exceeds that of most developed countries, we risk losing this advantage through continued neglect and apathy with respect to controlling the composition of gasoline and, therefore, the composition of vehicle emissions. Our standards are already 10-20 years behind those of countries such as the USA, Japan and the Scandinavian nations in several key areas (Furzer, 1994).

The failure to keep the legislation regarding the composition of Australian gasoline in line with recent developments and international recommendations can be attributed (at least partly) to the insular nature of the local oil refining industry and an over-reliance on overseas technology which has stifled local research and development activities. Consequently, the Australian public and environmental movements have failed to fully appreciate the decrease in air quality and fail to recognise the technological alternatives that are available to redress this problem. Local research has a valuable role in promoting these issues and can help to initiate change by identifying technically sound and economically viable approaches to reducing toxic emissions and improving air quality.

This study was also motivated by several technical issues. Hybrid reactive distillation is a relatively new development and there are still significant gaps in the current body of knowledge, particularly concerning specialised control strategies and the notable phenomenon of multiplicity. Although effective research has been completed on the

chemistry of reactive distillation and the control of conventional distillation, the intersection of these activities has attracted little prior attention. With expertise available in the associated areas, the current work was an opportunity to direct effort towards this aspect of reactive distillation using a combination of simulation and experimentation.

### **1.2.2 Objectives**

A relatively wide focus was assumed for this research to permit significant contributions to be made in several areas. In particular, an improved understanding of the behaviour of hybrid reactive distillation columns and the associated design issues will help to reduce the technical risk in developing this technology (especially locally), the study of control issues will allow for safer and more profitable operation of these columns and the experimental work will provide the basis for further work which should clearly demonstrate that this technology is both feasible and potentially profitable.

This thesis was undertaken with the objective of making technical contributions to the body of knowledge associated with fuel ether production in hybrid reactive distillation columns in the following areas:

- effective modelling techniques for both the steady state and dynamic simulation of reactive distillation columns;
- the understanding of obscure operating characteristics which are specific to reactive distillation;
- a design strategy for hybrid reactive distillation;
- the implications of extremely non-linear behaviour for the control of reactive distillation systems;
- the potential for multiple steady states in hybrid reactive distillation and the causes and implications of this phenomenon;
- the construction of pilot scale facilities for the synthesis of ETBE from ethanol and a locally available hydrocarbon source using non-commercial packing arrangements.

### 1.3 THESIS OUTLINE

Reactive distillation is a very broad topic and, although a wide range of issues are discussed in this thesis, the focus is exclusively on hybrid reactive distillation (i.e. reactive columns which include both reactive and non-reactive column sections) with application for the synthesis of fuel ethers. Specifically, the example of ETBE production is used to illustrate many of the salient points, and was the basis for much of the simulation study and the experimental work.

The thesis can be subdivided into three main topics: steady state simulation of reactive distillation and its implications for design (Chapters 3-6); dynamic simulation, including the study of dynamic effects such as multiplicity and hysteresis, and its application for control system design (Chapters 7-10); and experimental work on a reactive distillation pilot plant which has been constructed as part of this thesis (Chapters 11-12). Supplemental to this core are the literature review (Chapter 2), the conclusions and recommendations (Chapter 13) and the list of cited literature (Chapter 14).

The development of a satisfactory steady state model for reactive distillation requires attention to the fundamental behaviour of the system, including the reaction and phase behaviour, and this is discussed in Chapter 3 together with the principles behind the equilibrium stage model for distillation operations. The full reactive distillation column model is presented and then applied to the simulation of a MTBE column where experimental data was available and an ETBE column. Once the model is developed and validated, it can be used to study the behaviour of reactive distillation systems and to investigate attributes that differ from non-reactive distillation (Chapter 4). A steady state simulation model is also useful in formulating a design strategy for reactive distillation. Chapter 5 elaborates a design strategy and discusses the use of other tools for reactive column design, including reactive residue curves. It is important to integrate column design with global plant objectives to ensure that synergies are realised wherever possible and to maximise the profitability of the process equipment. This is discussed in Chapter 6 with reference to processing schemes, feed composition and process optimisation methods.

The extension of a steady state simulation model to the dynamic case is not trivial and the issues involved in this process are discussed in Chapter 7. The full dynamic model and examples of its application are also provided there. A dynamic simulation model is the ideal tool for control system design and invaluable in screening control configurations and examining transient process responses. Multiplicity is an inherently dynamic characteristic

and Chapter 8 shows how the full dynamic capability of the simulation models was accessed to identify transitions between parallel steady states and investigate the implications for control. However, it was important to ensure that the observed simulation behaviour was physically realisable and the distinction between events with practical significance and situations that can only be realised via simulation was also discussed. Chapter 9 describes how dynamic simulations were applied to conceive an acceptable regulatory control system for the ETBE column described earlier. The benefits of reactive distillation are intimately linked to the effectiveness of the operating policy and advanced control was shown to be important to minimise the effects of process disturbances. Chapter 10 discusses a method for concurrently controlling both principal operating objectives (ether purity and isobutene conversion) and an integrated control scheme that is flexible enough to handle a wide range of operating policies and economic criteria.

Chapters 11 and 12 describe the experimental apparatus that was constructed in conjunction with the simulation studies. The design of the experimental equipment focussed on the catalyst support and the packing design, both of which were original, and the control system. The commissioning of the pilot plant and tests which were undertaken to assess the effectiveness of the design are discussed in Chapter 12. An optimisation of the pilot plant operation and the collection of pilot plant data which would permit further commercialisation of this technology were not undertaken as part of this thesis.

Program listings for the simulation models (Chapters 3-10), calculations for the pilot plant design (Chapter 11) and raw experimental data (Chapter 12) have not been included in the thesis in order to conserve space. These are available from the School of Chemical Engineering, Curtin University of Technology, on request.

## **CHAPTER TWO**

### **HISTORICAL OVERVIEW**

- 2.1 Pertinent Research**
- 2.2 Reactive Distillation**
- 2.3 ETBE Synthesis**
- 2.4 Modelling Techniques**
- 2.5 Operability and Controllability Issues**
- 2.6 Summary**

#### **2.1 PERTINENT RESEARCH**

This thesis undertakes to study the simulation and control of reactive distillation, using ETBE synthesis as the primary example. This is a broad topic and pertinent research exists in four distinctly different areas. The previous work of process synthesists and design engineers on the development of reactive distillation is discussed in Section 2.2. The contributions of thermodynamicists are recognised in Section 2.3. Some relevant work has also been done by process modellers to develop steady state and dynamic model of reactive distillation and this is summarised in Section 2.4. Finally, the work of control theoreticians is considered in Section 2.5, particularly with regard to the identification and analysis of the multiplicity phenomena.

#### **2.2 REACTIVE DISTILLATION**

Reactive distillation represents the conjunction of conventional mixed-reactor technology and fractionation processes. The combination of these unit operations in a single vessel was first proposed in the 1920s (Keyes, 1932) but remained an obscurity until the 1980s. Since the 1930s, reactive distillation has been used in several specific applications but only with a homogenous catalyst. The use of heterogenous catalysts was first considered by Sennewald et al. (1971) but the potential of this development appears to have gone unrealised for another ten years.

A series of patents in the early 1980s (notably Smith, 1980a; 1980b; 1982) rejuvenated the technology by applying reactive distillation to the production of MTBE. Whereas earlier applications of reactive distillation were for specialty chemicals, MTBE was a commodity chemical and was about to enter a significant growth phase. The growth in demand for



MTBE was initiated by increasing environmental awareness and, later, boosted by legislative changes in the USA and elsewhere, but the shift from conventional technology to new reactive distillation processes was motivated by reduced capital cost and increased reactant conversion. The first reactive distillation process for MTBE production was in service by 1981 (Smith and Huddleston, 1982) and quickly gained industry acceptance.

The key developments which permitted the development of the MTBE reactive distillation process were methods for supporting small catalyst particles inside columns without creating hydraulic restrictions and for installing catalyst bales into large industrial columns. These breakthroughs were equally important for many other potential processes and initiated a significant increase in interest in reactive distillation which has continued into the 1990s.

Doherty and Buzad (1992) described three important commercial applications of reactive distillation (nylon 6,6, methyl acetate and MTBE) and referred to several other processes with the potential to benefit from reactive distillation (e.g. cumene, *tert*-butyl alcohol and alkylation). In each case, the use of reactive distillation increased either the selectivity or the conversion of the limiting reactant. Design methods for equilibrium chemical reactions and kinetically controlled reactions were proposed but the modelling techniques are not rigorous and not suitable for detailed design. It is also questionable whether they would find application for preliminary design given the complexity of the interactions between reaction and separation. A useful contribution of this work was the identification of three research opportunities (areas with little or no previous work): thermodynamics; simulation; and synthesis and design.

Around the same time, DeGarmo et al. (1992) produced a similar discussion of the general merits of reactive distillation without discussing any case studies. Potential advantages of reactive distillation were described but the main contribution was the elaboration of specific hardware requirements. Unfortunately, only a superficial coverage was given to the more technical issues and important details remained buried in the patent literature. In fact, little has been published on the properties of the various catalytic packings which suggests that the companies involved in this emerging area are relying on proprietary technology to maintain a competitive advantages. Yuxiang and Xien (1992a) presented several correlations for the mass transfer coefficients in a catalytic packed bed and were able to apply those results to a reactive distillation column operating with different fluids. More recently, Subawalla et al. (1997) provided some capacity and efficiency data for a catalyst bale, indicating an increasing openness in this area.

Experimental work on reactive distillation has been limited and, so far, contributed little useful data. Flato and Hoffman (1992) and Bravo et al. (1993) are the only cases which consider etherification reactions (e.g. MTBE, ETBE, TAME, etc.). Flato and Hoffman (1992) used a bench-top column with only stripping and reactive sections to produce MTBE from separate feed streams of mixed butenes and methanol. Their column included an automatic control system but yielded results which were inconsistent with viable industrial operation. Bravo et al. (1993) conducted experiments in a taller reactive column which contained a rectifying section as well as stripping and reactive sections. They considered TAME synthesis but were unable to produce a product purity or a reactant conversion which exceeded minimum acceptable targets for commercial columns. Gonzalez et al. (1997) investigated the preparation of *tert*-amyl alcohol in a pilot scale reactive distillation column and produced more worthwhile results, including an assessment of the reactive packing efficiency.

The interest in reactive distillation has recently triggered a further review of the industrial uses for this technology, and there is clearly significant potential for continued development. Podrebarac et al. (1997) produced a fairly comprehensive assessment of chemical syntheses which might benefit from reactive distillation and introduced several new applications (e.g. aldol condensation, hydrolysis of epoxides and olefin oligomerization). Rock et al. (1997) also discussed some novel applications of reactive distillation (e.g. selective hydrogenation and acetylene conversion) in an overview directed at the refining sector. Walker (1997) and Nathan (1997) highlighted the impact that reactive distillation is having on multi-national companies which have traditionally been heavy users of distillation by identifying two separate research projects which are sponsored by industry conglomerates. Although the advantages of this technology have been regularly elucidated, a disregard for the potential difficulties with the operation or implementation of reactive distillation is a common deficiency in all of the articles which are cited above.

Although the reactive MTBE process has been well documented, the application of reactive distillation to ETBE synthesis has remained relatively unexplored and is the subject of considerable attention here, notably Chapters 3, 4 and 6. This example is used to develop design methods (Chapter 5) which are suitable for other reactive distillation processes as well. The difficulties associated with developing and operating reactive distillation processes due to the increased process complexity which arises from the combination of reaction and separation in a single process are also addressed (e.g. Chapters 4, 5, 7 and 8). Finally, the experimental study (Chapter 11 and 12) will provide the basis for more detailed

studies of the capacity and efficiency of reactive distillation packings, thereby addressing another gap in the current literature.

## 2.3 ETBE SYNTHESIS

ETBE has recently emerged as an alternative gasoline additive to MTBE (Unzelman, 1989). ETBE has superior gasoline blending properties (Brockwell et al., 1991) and is considered partially renewable since it is produced from ethanol. The potential to utilise renewable resources increases the appeal of ETBE among environmental groups and has induced offers of substantial subsidies from some governments. It is considered that the two major obstacles which prevent the more widespread production of ETBE are: the cost of ethanol, which remains much higher than methanol in most market places; and a lack of information concerning its optimal production.

While MTBE synthesis has been researched extensively since the 1980s (e.g. Colombo et al., 1983; Rehfinger and Hoffman, 1990), the liquid-phase ETBE synthesis reaction appears not to have been studied in detail until the 1990s and data remains limited. However, several expressions for the reaction equilibrium constant are now available: Françoisse and Thyron (1991); Vila et al. (1993); Cunill et al. (1993); Jensen and Datta (1995); and, Gomez et al. (1997). The agreement between the various sets of data is generally good but the thermodynamic analysis of Jensen and Datta (1995) was more rigorous than the others, and their model is preferred overall. In most cases, the UNIFAC method was used to generate the necessary estimates of thermodynamic properties. This is considered appropriate given the conformity of the predictions with the available experimental data.

Kinetic models of the ETBE reaction have been proposed by Fité et al. (1994) and Jensen and Datta (1996). These models differ significantly with respect to the methodology that was used. Jensen and Datta (1996) considered a more general case and produced a sound reaction model that is not reliant on simplifying assumptions concerning the rate limiting step (i.e. ethanol adsorption). Consequently, their reaction rate expression is valid over a wider range of compositions and temperatures and is preferred for most applications. The model is somewhat complex but simplifications can be implemented without difficulty to yield a less numerically intensive model where necessary.

The commercial production of ETBE has been discussed infrequently in the open literature. Brockwell et al. (1991) recommended a similar process to that which is used for conventional MTBE production, with the possible addition of equipment to deal with the

azeotrope which forms between ethanol and water in the ethanol recovery. They did not consider the use of reactive distillation for ETBE production. Matouq et al. (1996) discussed a novel process for ETBE synthesis from low-grade alcohol using reactive distillation but the viability of their proposal appears marginal. Regular reviews of licensed processes also suggest that the process scheme which is used to produce MTBE can be applied equally to ETBE production but there is insufficient data in these reports to determine the accuracy of these claims (e.g. CDTECH, 1995; Hüls AG, 1995).

## 2.4 MODELLING TECHNIQUES

Two fundamentally different approaches to simulating distillation systems have been developed: the equilibrium stage model and the non-equilibrium, transfer rate model (Kister, 1992). Theoretically, both of these methods can be applied to reactive distillation with appropriate modifications and additions to reflect the reaction.

The steady state simulation of reactive distillation has been tackled frequently since the 1970s. Simandl and Svrcek (1991) provided an excellent review of the work in this area and alluded to the range of numerical methods that can be applied to solve the system of equations which describe the reactive column. Their survey indicated that only the equilibrium stage model had been used to that point.

Yuxiang and Xien (1992b) considered the rate-based approach and produced a steady state model of a reactive MTBE column. The primary advantage of this approach is that equipment dimensions and packing (or tray) characteristics can be accounted for within the model so that a more realistic view of the column is afforded. However, this is more than offset by the increased demand on empirical constants and the much larger number of equations that must be solved. To support their methodology, Yuxiang and Xien conducted experiments to determine mass transfer coefficients and some other properties. They were able to show that the rate-based approach yields almost identical results to the equilibrium stage model provided sufficient detail is included in the model but did not demonstrate any advantage with respect to model accuracy or efficiency.

Sundmacher and Hoffman (1996) also developed a rate-based model of a reactive distillation process but used correlations instead of experiments to find the necessary mass transfer parameters. They attempted to validate their model with experimental data but the agreement between the model and the experimental was weak and they provided insufficient data to fully assess the effectiveness of their model.

Grosser et al. (1987) proposed a simplified non-steady state model of reactive distillation for a nylon 6,6 column but their assumption of constant molar overflow in the vapour phase is considered unrealistic for most systems, including MTBE and ETBE processes. More recently, several rigorous dynamic models have been proposed for simulating transient events and investigating process dynamics of reactive distillation. Abufares and Douglas (1995) proposed a model based on the equilibrium stage approach that included expressions to account for tray hydraulics and reaction kinetics. They successfully demonstrated the validity of this approach by comparing simulation results to previously published experimental results from a laboratory scale column. Ruiz et al. (1995), Schrans et al. (1996) and Pilavachi et al. (1997) have subsequently produced dynamic models with a similar structure and have shown that these models can be used effectively for reactive MTBE columns although limited data has been provided for model validation.

Alejski and Duprat (1996) provided a comprehensive review on reactive distillation simulation and also proposed a rigorous dynamic model of their own which they subsequently applied to a reactive ethyl acetate column. The most important contribution of this work was to compare dynamic models of varying complexity to determine whether various simplifying assumptions were valid or invalid. They concluded that it was necessary to model the hold-up on each stage (e.g. using the Francis weir formula) where the hold-ups are large, but simpler models are acceptable where the hold-ups are smaller and the dynamics are much faster.

The application of ETBE reaction chemistry to reactive distillation appears not to have been considered previously. However, the modelling techniques used previously, particularly the equilibrium stage model, appear to be sound, and appropriate equilibrium and kinetic expressions for the ETBE reaction are available (Section 2.3). This approach is developed in Chapters 3 and 6 for steady state and dynamic problems, respectively. The experimental equipment described in Chapters 11 and 12 will also provide the basis for more detailed validation of the modelling techniques.

## 2.5 OPERABILITY AND CONTROLLABILITY ISSUES

The operability of reactive distillation processes has received little direct attention in the literature but the recent discovery of multiple steady states in a reactive MTBE column (Jacobs and Krishna, 1993; Nijhuis et al., 1993) has significant implications for both the operation and control of these columns. Jacobs and Krishna (1993) and Nijhuis et al. (1993) appear to have collaborated in their research as they studied the same column configuration and produced similar results. Neither group was able to adequately determine the cause of the observed behaviour but their investigations made an important contribution in refuting several hypotheses, including CSTR multiplicity, the exothermic nature of the reaction, and crossing non-reactive distillation boundaries via the reaction.

Although the citations indicated above were the first reports of multiple steady states in reactive distillation, a similar phenomenon had already been discovered for ideal binary distillation (Jacobsen and Skogestad, 1991) and extensively studied with respect to azeotropic distillation (e.g. Kienle and Marquardt, 1991; Laroche et al., 1992; Bekiaris et al., 1993). The results of Jacobsen and Skogestad (1991) were of seminal importance: they provided examples of multiplicity, a thorough theoretical analysis of those results, derived recommendations from their analysis and presented two fundamentally sound explanations for the observed behaviour. Later papers from the same authors (e.g. Jacobsen and Skogestad, 1994; 1995) extended the original results and addressed operability and controllability issues more directly.

Bekiaris et al. (1993) considered only azeotropic distillation and proposed a different approach to the analysis of columns which exhibit multiple steady states. They developed a geometrical tool which could be applied to ternary composition diagrams to predict the product compositions and flow rates for any given feed composition provided that the column operated with perfect fractionation (infinite number of stages and infinite reflux ratio; the  $\infty/\infty$  analysis). Bekiaris and Morari (1996) reviewed these results to explain the implications for design and provide limited predictions for multiplicity in ternary systems using only VLE data (i.e. the composition of azeotropes). This work was important but disregarded other possible causes of multiple steady states and addressed a restricted range of column control configurations.

Recently, Güttinger and Morari (1997) extended the original results of Bekiaris et al. (1993) so that the technique could be applied to homogenous reactive distillation. The tool was applied to the hybrid reactive distillation of MTBE and produced some promising results but

the extrapolation of  $\infty/\infty$  predictions to finite columns is uncertain and the tool cannot be used if a constant internal column flow (e.g. the reflux or boilup rate) or a duty specification is required.

Hauan et al. (1995; 1997) also attempted to address the problem of multiple steady states in reactive distillation, and focussed on the column that Jacobs and Krishna (1993) and Nijhuis et al. (1993) had analysed. They presented a mechanistic explanation of the behaviour but provided only a single example (i.e. the recreation of previously published results) to support their hypothesis and were unable to demonstrate its validity. Their explanation is flawed in some crucial areas (e.g. the discussion of azeotropic behaviour and relative volatilities) and includes references to irrelevant data (e.g. activity coefficient profiles) which further confuse their postulations. Their contentions are tenuous (at best) and directly contradict those of Jacobs and Krishna (1993) who tested their conclusions with more rigour and provided examples to support their claims. *(Note: Hauan et al. (1995) gave their paper a catchy title which ultimately proved to be more important than the weaknesses identified above since their paper was eventually published three times in essentially the same form!)*

Schrans et al. (1996) also analysed a similar MTBE column to that which was originally described by Jacobs and Krishna (1993). Their contribution was to extend the modelling to transient responses and they were able to show a transition between parallel steady states, indicating that both the high and low conversion steady states are simultaneously accessible. Unfortunately, other results reported by these authors serve to confuse rather than clarify the issue of reactive distillation multiplicity since the important distinction between input multiplicity (i.e. multiple sets of inputs producing the same set of outputs) and output multiplicity (i.e. multiple sets of outputs from a unique set of inputs) was overlooked.

Ciric and Miao (1994) considered a different problem: multiple steady states in the reactive distillation of ethylene glycol. They used a homotopy continuation method to construct bifurcation curves which showed up to nine multiple steady states. They tested a range of hypotheses for the observed multiplicity but were unable to find a consistent and comprehensive mechanism.

Subsequent to the simulation studies of multiple steady states in ideal binary distillation, azeotropic distillation and reactive distillation, the natural question of experimental evidence for the phenomenon was addressed. Sundmacher and Hoffman (1995) completed experiments on a bench-top reactive distillation column for MTBE synthesis and found oscillatory behaviour but could not confirm multiple stable steady states. Kienle et al.

(1995) and Koggersbøl et al. (1996) experimented with the ideal binary separation of methanol and propanol, and both groups were able to produce results which supported previous simulation studies and confirmed the presence of multiple steady states in that system. Güttinger et al. (1997) performed two sets of distillation experiments on an azeotropic system and were able to produce results which were consistent with simulations and with  $\infty/\infty$  predictions. Thus, the presence of multiple steady states in distillation has become irrefutable.

Conclusive experimental evidence for multiple steady states in reactive distillation does not yet exist but there seems little reason to doubt that convincing results are forthcoming since the multiplicity phenomenon has been demonstrated for other systems. However, the significance of the simulation results is somewhat equivocal since many of the reports of multiplicity (e.g. Jacobs and Krishna, 1993; Nijhuis et al., 1993; Hauan et al., 1995; 1997; Schrans et al., 1996; Mohl et al. 1997; etc.) rely on an imposed requirement for a physically unrealisable condition (e.g. a constant molar flow). This crucial weakness suggests that simulation efforts should be redirected and creates a new motivation for experimentation.

The design of control schemes for distillation processes is an established area of research but there is little evidence of direct attempts to design controllers specifically for reactive distillation. Jacobsen and Skogestad (1995) addressed some issues concerning the control of columns which exhibit multiple steady states but did not consider possible reactive distillation.

Multiple steady states in the reactive distillation of ETBE and MTBE are analysed thoroughly in Chapter 8, considering predominantly physically realisable conditions. Mechanisms for this phenomenon are also developed and unite the postulations of several research groups. The implications for this unusual behaviour are addressed with respect to design and operation (Chapter 8) and control (Chapter 10). The substantial issue of specific control applications for reactive distillation is also discussed extensively in Chapters 9-10. Once again, the experimental work (Chapter 11 and 12) provides the basis for further study and an ideal platform to develop experimental evidence for multiple steady states in reactive distillation and to test control systems practically.



## 2.6 SUMMARY

The potential applications of reactive distillation have been discussed extensively in the literature but it appears that ETBE synthesis has not been considered specifically. Studies of MTBE synthesis via reactive distillation and the inherent similarities between the MTBE and ETBE systems suggest that reactive distillation could be used to improve the reactant conversion and reduce the capital cost of ETBE synthesis equipment. However, ETBE production has not been investigated sufficiently to determine if there are specific design or operating requirements that make the synthesis unique. Practical and effective design methods for reactive distillation are required and further experimentation on reactive packings is warranted.

The thermodynamics and kinetics of the ETBE synthesis reaction have been studied sufficiently to provide satisfactory expressions for the equilibrium constant, rate constant and to develop a detailed model of the reaction. The information that is now available is in good order and suitable to be implemented within simulation models for reactors or reactive distillation.

There are examples in the literature of both steady state and dynamic models of reactive distillation, for several systems including MTBE synthesis. The majority of models utilise the equilibrium stage approach and the validity of the technique has been confirmed via comparisons of simulation results and experimental data. Rate-based modelling has also been attempted but the results indicate that the additional model complexity and the increased requirement for parametric data (e.g. mass transfer coefficients) are not justified by the superior realism which the approach engenders.

The subject of multiple steady states in reactive distillation has been widely covered in the literature and parallel investigations of ideal binary distillation and azeotropic distillation have significant implications for continuing research in this area. However, despite the recent attention, comprehensive and consistent explanations for all types of multiplicity have proved elusive. Clearly, further work is required to adequately explain and predict multiplicities for industrial purposes (e.g. the design, operation and control of reactive distillation columns).

Reports of experimental work on MTBE synthesis via reactive distillation have been restricted to bench-top equipment and there appears to have been no work on ETBE synthesis. Experimental studies are also required to validate the experimental evidence of

multiple steady states in reactive distillation. The control of reactive distillation processes has been essentially ignored in the literature and the implications for operability and controllability of combining unit operations (i.e. reactor and separator) appears not to have been considered to date.

## CHAPTER THREE

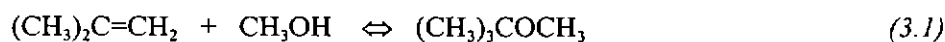
### STEADY STATE SIMULATION

- 3.1 Reaction System Chemistry**
  - 3.1.1 Reaction Models and Mechanisms
  - 3.1.2 Physical Properties
  - 3.1.3 Phase Behaviour
- 3.2 Reactive Distillation Model**
  - 3.2.1 Column Configuration
  - 3.2.2 Reactive Stage Model
  - 3.2.3 Non-Reactive Stage Model
  - 3.2.4 Feed Stage Model
  - 3.2.5 Condenser Model
  - 3.2.6 Reboiler Model
  - 3.2.7 Thermodynamic Methods
  - 3.2.8 Simulation Packages
- 3.3 Primary Model Validation**
- 3.4 ETBE Simulations**
  - 3.4.1 ETBE Column Simulation Basis
  - 3.4.2 ETBE Column Simulation Results

### 3.1 REACTION CHEMISTRY

#### 3.1.1 Reaction Models and Mechanisms

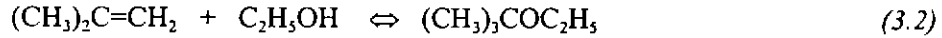
Short-chained tertiary olefins can be reacted with short-chained alcohols to form a sub-class of tertiary ethers that have been conveniently designated as *fuel ethers*. These ethers have useful properties for inclusion in gasoline blends: a high specific energy, a high octane number, a relatively low volatility and oxygen to encourage cleaner burning (Piel and Thomas, 1990). The simplest fuel ether is methyl *tert*-butyl ether, MTBE, which is derived from isobutene and methanol:



The reaction requires an acid catalyst to proceed usefully. Protonated ion exchange resins (e.g. Amberlyst 15™) are the most widely used (Jensen, 1995) although experiments have also been conducted with zeolites (e.g. HZSM-5) and sulphur-roasted zircon oxides (Collignon et al., 1997; Quiroga et al., 1997). The reaction is reversible and equilibrium limited in the industrially significant range of temperatures. The reaction details are well

understood: the equilibrium constant has been determined as a function of temperature (e.g. Rehfinger and Hoffman, 1995; Zhang and Datta, 1996) and the reaction kinetics have been fitted to a Langmuir-Hinshelwood-Hougen-Watson (LHHW) model (Zhang and Datta, 1996).

The chemistry of ethyl *tert*-butyl ether, ETBE, is inherently similar to MTBE. The analogous reaction is:



The reaction is more strongly limited by equilibrium so that the equilibrium conversion from a stoichiometric mixture of reactants at 70°C is only 84.7%. The reaction equilibrium constant (Jensen and Datta, 1995) is given by:

$$\begin{aligned} \ln K_{ETBE} = 10.387 + \frac{4060.59}{T} - 2.89055 \ln T - 0.0191544T \\ + 5.28586 \times 10^{-5} T^2 - 5.32977 \times 10^{-8} T^3 \end{aligned} \quad (3.3)$$

Jensen (1996) also developed a kinetic model for the reaction, utilising another LHHW model. The model pertains to activities (not concentrations) in order to account for the considerable liquid phase non-ideality and uses the UNIFAC method to estimate activity coefficients. The proposed reaction mechanism involves two adsorbed ethanol sites reacting with one adsorbed isobutene site in the rate-determining step, giving a total of three active sites. The rate equation derived from this model (equations 3.4-3.6) produced a better fit with the experimental data than other models. However, a simplified model (equations 3.7-3.8) is applicable for ethanol concentrations less than 4.0 mol%.

$$r_{ETBE} = \frac{m_{cal} \cdot k_{rate} \cdot a_{EtOH}^2 \left( a_{iBuI} - \frac{a_{ETBE}}{K_{ETBE} \cdot a_{EtOH}} \right)}{(1 + K_A \cdot a_{EtOH})^3} \quad (3.4)$$

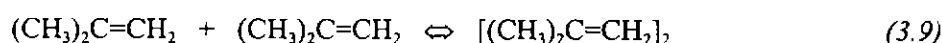
$$\ln K_A = -1.0707 + \frac{1323.1}{T} \quad (3.5)$$

$$k_{rate} = 7.418 \times 10^{12} \exp\left(-\frac{60.4}{RT}\right) \quad (3.6)$$

$$r_{ETBE} = m_{cat} \cdot k_{rate} \cdot \left( \frac{a_{iBut}}{a_{EtOH}} - \frac{a_{ETBE}}{K_{ETBE} \cdot a_{EtOH}^2} \right) \quad (3.7)$$

$$k_{rate} = 1.209 \times 10^{12} \exp\left(-\frac{87.2}{RT}\right) \quad (3.8)$$

The dimerisation of isobutene to form di-isobutene (DIB) is an unavoidable side reaction in both the ETBE and MTBE reaction systems:



This reaction is also equilibrium limited and an expression for the equilibrium constant of the dimerisation has been estimated from the free energies of formation (Columbo et al., 1983):

$$\ln K = 95.2633 + 5819.8644/T - 17.2 \ln T - 0.0356 T \quad (3.10)$$

If any water is present in the reaction environment, one further, undesirable reaction (the hydration of isobutene to form of isobutanol) is also possible:



The ETBE rate equations clearly show that ethanol has a retarding effect on the reaction. However, in practice, some ethanol excess is required to limit the side-reactions involving isobutene. The LHHW reaction model predicts a large adsorption equilibrium constant for ethanol that implies that, at ethanol excesses of 4 mol% and above, the catalyst surface is largely covered with ethanol. Under these conditions, the dimerisation and oligomerisation of isobutene are essentially eliminated (Kitchaiya and Datta, 1995).

The reaction rate also depends on the activity of the catalyst that is susceptible to both deactivation (slow ageing) and poisoning (fast ageing). Poisoning is potentially a serious problem as water and, especially salts, neutralise active catalyst sites. Deactivation occurs over a much longer period and is accelerated by thermal degradation caused by hot spots due to inadequate mixing. *In situ* regeneration has generally been unsuccessful and a regular catalyst changeover is required for most reactors (Flato and Hoffman, 1992).

### 3.1.2 Physical Properties

The reaction components have distinctly different physical properties and form a very non-ideal mixture. The most relevant properties are summarised in Table 3.1 (SimSci, 1994; Furzer, 1994; Brockwell et al., 1991; Lide, 1995). In an industrial context, isobutene is only likely to be available as a component within a mixture of other hydrocarbons (mostly C<sub>4</sub>s) but for most practical purposes, the physical properties of the mixture can be lumped and approximated with the properties of isobutene. While both ethanol and ETBE can be stored at atmospheric pressure, neither isobutene nor mixtures of the three components can unless the percentage of ETBE in the mixture is substantial.

Table 3.1 - Key Physical Properties of the Reaction Components

Property	Ethanol	Isobutene	ETBE
Molecular Weight	46	56	102
Specific Gravity	0.795	0.600	0.746
Normal Boiling Point (°C)	78	-7	73
Boiling Point @ 1000 kPa (°C)	155	75	174
Blending RVP (kPa)	122	440	27
Specific Heat (kJ/kg)	2.46	1.27	2.10
Octane Rating ( $(RON+MON)/2$ )	115	n/a	111
Energy Content (MJ/kg)	26.7	44.6	36.3

The values of octane are approximate (literature reports vary but ETBE is generally claimed to have an average octane rating one number higher than MTBE: Furzer, 1994; Brockwell et al. 1991; Piel and Thomas, 1990; Unzelman, 1989) and vary with the composition of the mixture. Knock engine testing is required to confirm the octane properties of a mixture. An octane rating is not generally cited for isobutene due to its high volatility but a high blending value (approximately 100) is anticipated based on iso-olefin trends.

### 3.1.3 Phase Behaviour

The combination of an alcohol, an olefin and an ether forms a highly non-ideal liquid phase and azeotropes have been detected experimentally in the ETBE reaction system and other similar mixtures (Gmehling, 1994). The UNIFAC model predicts the presence of these azeotropes and was found to be accurate in estimating their compositions. This is useful to expand on the limited experimental data and to determine the effect of pressure on the azeotropic compositions. Table 3.2 describes the phase behaviour of three binary pairs in the ETBE system. Importantly, the azeotropes between ethanol and butenes appear to only exist at high pressure. All of the azeotropes are predicted to be homogenous.

**Table 3.2 - Compositions of Binary Azeotropes in the ETBE Reaction System**

Binary Pair	Ethanol Conc. at 0 kPag (mol%)		Ethanol Conc. at 950 kPa (mol%)		Ethanol Conc. at 1400 kPa (mol%)	
	Exp't	UNIFAC	Exp't	UNIFAC	Exp't	UNIFAC
ethanol- isobutene	n/a	-	n/a	-	0.94%	1.25%
ethanol- 1-butene	n/a	-	n/a	-	n/a	1.45%
ethanol- ETBE	37%	38%	n/a	59%	n/a	66%

The phase behaviour of the MTBE system departs from the above in several important aspects: the azeotropes between methanol and the various butenes exist at nearly all pressures; these azeotropes contain a much larger percentage of methanol (7-15 mol%); and UNIFAC predicts phase splits between methanol and the various butenes at atmospheric pressure. Such a phase split has not been reported but direct experimentation is made difficult by the low temperatures required. However, this uncertainty is relatively unimportant as the model is still consistent with industrial experience of homogeneity at pressure and the system can be easily constrained to a single liquid phase by specifying vapour-liquid-equilibrium (VLE) rather than vapour-liquid-liquid-equilibrium (VLLE).

The MTBE system has been modelled with other thermodynamic packages (e.g. the Wilson equation, Bravo et al., 1993; and the UNIQUAC method, Abufares and Douglas, 1995) but the UNIFAC method is recommended, regardless of the accuracy of the predictions of any liquid phase splits, for its superior accuracy in predicting azeotropic compositions. Although the choice of VLE or VLLE makes little difference for the ETBE system, a VLE model is recommended for MTBE as the azeotropic compositions are predicted much more precisely than with a VLLE model.

## 3.2 REACTIVE DISTILLATION MODEL

### 3.2.1 Column Configuration

Reactive distillation columns for fuel ether synthesis are actually hybrid columns consisting of three distinct sections. The reactive section is located between two non-reactive column sections that separate the reactants from the product. This configuration is shown in Figure 3.1. The stripping section purifies the ether product and recycles unreacted reactants to the reactive section. The rectifying section is required to prevent the loss of ether in the distillate. The combined action of the non-reactive sections produces a composition within

the reaction section that promotes the forward (synthesis) reaction in favour of the backward (decomposition) reaction by Le Chatelier's principle.

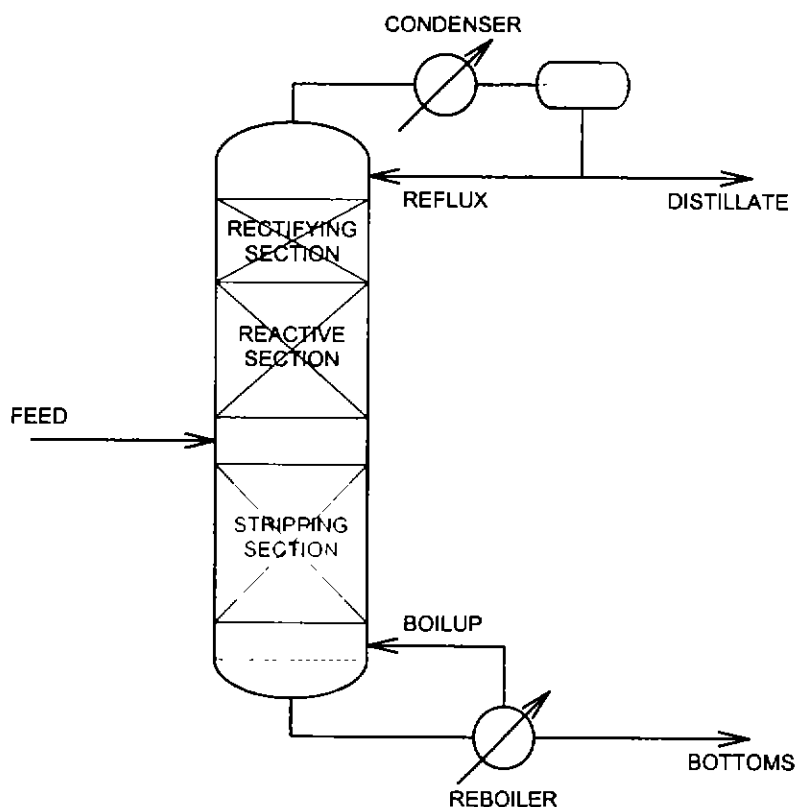


Figure 3.1 - Hybrid Reactive Distillation Column for Ether Synthesis

### 3.2.2 Reactive Stage Model

Distillation systems have traditionally been modelled as a series of equilibrium stages using the MESH (Material balance, vapour-liquid Equilibria, mole fraction Summations and Heat balance) equations. The main alternative is the rate based mass transfer model that is implemented with the MERQ (Material balance, Energy balance, Rate equations for mass transfer and phase eQuilibrium at the vapour-liquid interface) equations. The rate-based approach is gaining in popularity but it requires the estimation of a large number of empirical and semi-empirical parameters and the complex array of equations the model generates demands significant computational power. These models are not yet any more accurate than simulations using the equilibrium model although there is undoubted potential to reflect reality more closely. Where experimental data is readily available to estimate mass transfer coefficients and the column geometry is well known and easily definable algebraically, the rate-based approach is a viable alternative. However, the equilibrium stage model (modified with efficiency parameters, if necessary) remains the best choice in most cases and is still the clearly preferred modeling technique in both industry and academia.



The absence of the requisite data for rate based modelling compelled the development of a reactive distillation model using the equilibrium stage approach. Equations (3.12)-(3.26) describe the reactive stage shown in Figure 3.2. The reaction is modelled rigorously using the equilibrium and kinetic data from equations (3.3), (3.7) and (3.8). The construction of the equations is such that the heat of reaction is calculated implicitly and does not need to be separately specified. The principal side-reaction (dimerisation) is modelled as an equilibrium reaction while the other side-reactions are considered negligible. The ETBE reaction is fast and proceeds close to equilibrium with only a modest catalyst loading so that the assumption of reaction equilibrium introduces little error in many simulations. A simplified model that assumes reaction equilibrium (or an infinite supply of catalyst) replaces equations (3.16), (3.18) and (3.19) with equation (3.27).

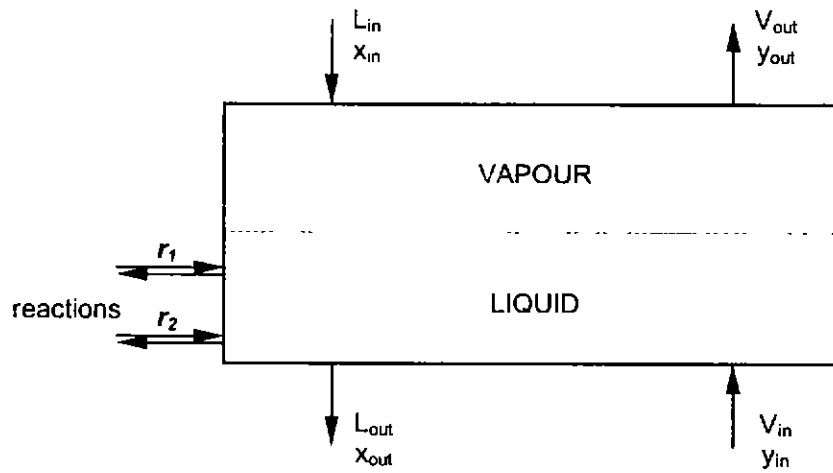


Figure 3.2 - A Reactive Equilibrium Stage

$$L_{in} + V_{in} - L_{out} - V_{out} + \sum r_{1,i} + \sum r_{2,i} = 0 \quad (3.12)$$

$$r_{1,ETBE} = -r_{1,EtOH} = -r_{1,iBuT} \quad (3.13)$$

$$r_{2,DIB} = -2r_{2,iBuT} \quad (3.14)$$

$$r_{1,nBuT} = r_{1,DIB} = r_{2,ETBE} = r_{2,EtOH} = r_{2,nBuT} = 0 \quad (3.15)$$

$$r_{1,ETBE} = \frac{m_{cat} \cdot k_{rate} \cdot a_{EtOH}^2 \left( a_{iBuT} - \frac{a_{ETBE}}{K_{ETBE} \cdot a_{EtOH}} \right)}{(1 + K_A \cdot a_{EtOH})^3} \quad (3.16)$$

$$\ln K_{ETBE} = 10.387 + \frac{4060.59}{T} - 2.89055 \ln T - 0.0191544T + 5.28586 \times 10^{-5} T^2 - 5.32977 \times 10^{-8} T^3 \quad (3.17)$$

$$\ln K_A = -1.0707 + \frac{1323.1}{T} \quad (3.18)$$

$$k_{rate} = 7.418 \times 10^{12} \exp\left(-\frac{60.4}{RT}\right) \quad (3.19)$$

$$\ln K_{DIB} = 95.2633 + \frac{5819.26}{T} - 17.2 \ln T - 0.0356T \quad (3.20)$$

$$L_{in}x_{i,in} + V_{in}x_{i,in} - L_{out}x_{i,out} - V_{out}x_{i,out} + r_{1,i} + r_{2,i} = 0 \quad (3.21)$$

$$L_{in}H_{i,in}^L + V_{in}H_{i,in}^V - L_{out}H_{i,out}^L - V_{out}H_{i,out}^V = 0 \quad (3.22)$$

$$P \cdot y_i = \gamma_i \cdot x_i \cdot P_i^{vap} \quad (3.23)$$

$$T^V = T^L \quad (3.24)$$

$$P = P_{in}^V \quad (3.25)$$

$$\sum y_i = 1 \quad (3.26)$$

$$K_{ETBE} = \frac{a_{tBE}}{a_{tBu} a_{EtOH}} \quad (3.27)$$

It is important to note that the pressure drop across the equilibrium stage is not calculated. Therefore, the column is assumed to operate with a fixed pressure profile. Similarly, these equations assume no accumulation on each stage so that liquid (or vapour) holdup is not calculated. However, constant molal overflow has **not** been assumed so that the composition changes resulting from VLE **and** the reactions will affect the flows of both liquid and vapour.

### 3.2.3 Non-Reactive Stage Model

Non-reactive stages (i.e. stages in the rectifying and stripping sections) can be modelled on the same basis as the reactive stages except that the reaction inputs to the liquid phase ( $r_1$  and  $r_2$ ) do not need to be considered. The simplified set of equations resulting from setting  $r_{1,i} = 0$  are given by equations (3.28)-(3.34).

$$L_{in} + V_{in} - L_{out} - V_{out} = 0 \quad (3.28)$$

$$L_{in}x_{i,in} + V_{in}x_{i,in} - L_{out}x_{i,out} - V_{out}x_{i,out} = 0 \quad (3.29)$$

$$L_{in}H_{i,in}^L + V_{in}H_{i,in}^V - L_{out}H_{i,out}^L - V_{out}H_{i,out}^V = 0 \quad (3.30)$$

$$P \cdot y_i = \gamma_i \cdot x_i \cdot P_i^{vap} \quad (3.31)$$

$$T^V = T^L \quad (3.32)$$

$$P = P_{in}^v \quad (3.33)$$

$$\sum y_i = 1 \quad (3.34)$$

### 3.2.4 Feed Stage Model

The feed stage is simply a non-reactive (or reactive) stage with an additional input that alters the form of the mass and energy balances. The resulting equations are:

$$F + L_{in} + V_{in} - L_{out} - V_{out} = 0 \quad (3.35)$$

$$Fz + L_{in}x_{i,in} + V_{in}x_{i,in} - L_{out}x_{i,out} - V_{out}x_{i,out} = 0 \quad (3.36)$$

$$FH^F + L_{in}H_{i,in}^L + V_{in}H_{i,in}^V - L_{out}H_{i,out}^L - V_{out}H_{i,out}^V = 0 \quad (3.37)$$

$$P \cdot y_i = \gamma_i \cdot x_i \cdot P_i^{vap} \quad (3.38)$$

$$T^v = T^L \quad (3.39)$$

$$P = P_{in}^v \quad (3.40)$$

$$\sum y_i = 1 \quad (3.41)$$

### 3.2.5 Condenser Model

The condenser model can be considered a special case of the non-reactive stage model. The configuration in Figure 3.1 shows a total condenser (i.e. no vapour phase product) and two liquid-phase products (i.e. reflux and distillate), and the material balance equations (3.42 and 3.43) must be modified to reflect this. The heat removal rate must be accounted for in the model and the energy balance equation (3.44) was modified accordingly. In order for the column pressure to be linked to the condenser duty, the equilibrium relationship (equation 3.45) was also modified. This allows the pressure to be fixed at the condenser and for this value to be propagated down the column without creating a numerical problem which can arise with other approaches.

$$V - L_1 - L_2 = 0 \quad (3.42)$$

$$V y_i - L_1 x_{1i} - L_2 x_{2i} = 0 \quad (3.43)$$

$$V H^v - L_1 H_1^L - L_2 H_2^L - Q_c = 0 \quad (3.44)$$

$$P = \sum \gamma_i \cdot y_i \cdot P_i^{vap} \quad (3.45)$$

### 3.2.6 Reboiler Model

The reboiler was also modelled as a modified equilibrium stage. Figure 3.1 shows a partial reboiler with both a vapour and a liquid product and this is reflected in the material balance equations (3.46-3.47). The energy balance equation (3.48) must be altered to include the reboiler duty but the equilibrium relationships (equations 3.49-3.52) are the same as the non-reactive stage model.

$$L_{in} - L_{out} - V_t = 0 \quad (3.46)$$

$$L_{in} x_{i,in} - L_{out} x_{i,out} - V y_i = 0 \quad (3.47)$$

$$L_{in} H_{in}^L - L_{out} H_{out}^L - V H^V + Q_r = 0 \quad (3.48)$$

$$P \cdot y_i = \gamma_i \cdot x_i \cdot P_i^{vap} \quad (3.49)$$

$$T^V = T^L \quad (3.50)$$

$$P = P_{in}^V \quad (3.51)$$

$$\sum y_i = 1 \quad (3.52)$$

### 3.2.7 Thermodynamic Methods

Equations (3.12)-(3.52) fully describe the reactive distillation column but additional equations and numerical routines are required to determine the parameters of this model. Geometrical parameters are not required as the flow properties (i.e. pressure drop and holdup) are not modelled but several physical properties are required. Vapour pressures were estimated from liquid temperatures using Antoine equations fitted to recent experimental data (Krähenbühl and Gmehling, 1994; Gmehling and Onken, 1977; Dean, 1992; Reid et al., 1987). The UNIFAC model was used to estimate activity coefficients in order to be consistent with the reaction model and to provide the most accurate representation of the phase behaviour. Enthalpies and densities were estimated from liquid or vapour phase temperatures using the Soave-Redlich-Kwong (SRK) method. The SRK equations are recommended for hydrocarbon systems at moderate temperature and pressure although similar equation-of-state methods (eg. Peng-Robinson) would have been equally acceptable. Although these methods often provide inaccurate density predictions, this was of little consequence here because mass and molar flow rates are used exclusively in the subsequent analyses. An ideal vapour phase was assumed due to the modest pressure.

### 3.2.8 Simulation Packages

The reactive distillation model described above was implemented directly in SpeedUp (Aspen Tech 1993) and indirectly in Pro/II (SimSci, 1994), both of which are commercial

process simulators. SpeedUp is an equation-based simulator that is sufficiently flexible to permit equations to be input in any form provided that consistency constraints are honoured and the model conforms to the simulator's syntax and structure requirements. The global system of equations for the full model contained a total of 578 variables and 504 linear and non-linear equations. Importantly, this model could be updated and modified for the analysis of dynamic responses. However, the numerical solution of this set of equations required very good initial estimates of the system outputs. This reduces the robustness of the solution method (but not of the model itself) and requires the initial solution to be found by slowly building the full model in stages, saving the entire output matrix after each stage for use in solving the next stage.

Pro/II is a sequential modular simulation package that contains an extensive model library that allows most unit operations to be simulated easily and accurately. It allows the property methods and reaction details to be specified and provides some control over solution methods but requires the use of the default unit operation equations. This simplifies the simulation task but somewhat restricts its range of applicability. The ease of development and robustness of the model were distinct advantages of using Pro/II but its deficiencies compelled the use of SpeedUp in some cases. Specifically, convergence was found to be unlikely when the reaction kinetics were modelled fully rigorously although SpeedUp can handle this case provided the equation structure is correct. This facility of SpeedUp was used to test the assumption of chemical equilibrium in the Pro/II simulations. A moderate catalyst loading was found to produce an isobutene conversion of only 0.2-0.3% less than the equilibrium conversion - an acceptable result. On the other hand, Pro/II was the better tool for checking the assumption of an ideal vapour phase. A fugacity coefficient model can be easily implemented within Pro/II by specifying a change in the thermodynamic routines being used. The fugacities were found to be generally within 0.5% of the partial pressures - an acceptable result which again confirms the validity of the original assumption.

### 3.3 PRIMARY MODEL VALIDATION

To validate the reactive distillation model without experimental data, Smith's MTBE column was simulated for the case described in his patent application (Smith, 1980) using both Pro/II and SpeedUp. The numbers of rectification, reaction and stripping stages were based on previous estimates (Abufares and Douglas, 1995). The model described by equations (3.12)-(3.27) and (3.29-3.52) has three degrees of freedom (excluding the feed definition and the mass of catalyst on each reactive stage): the column pressure and two product specifications. Where uncertainty exists in the system inputs, the choice of product specifications can significantly affect the results but an appropriate combination of specifications (e.g. one external flow rate and one internal flow rate) can minimise the effect of the uncertainty. In this case, the bottoms flow rate (determined implicitly from the patent results) and the reflux ratio (given explicitly in the patent application) were specified. Table 3.3 compares the simulation results, obtained with both Pro/II and SpeedUp using the equation structure and physical property routines described above, with the limited experimental data from the patent application.

Table 3.3 - Simulation Results and Experimental Data for Smith's MTBE Column

Property	Pro/II	SpeedUp	Experimental
Condenser Temperature (°C)	61.0	64.6	n/a
Reaction Zone Temperature (°C)	69.0	70.1	71
Reboiler Temperature (°C)	128.0	125.7	127
Isobutene Conversion (mol%)	91.6	91.6	91
Bottoms MTBE Purity (mol%)	92.2	92.6	91.9
DIB Bottoms Concentration (mol%)	1.2	0.9	6.1
Condenser Duty (kW)	2.14	1.99	n/a
Reboiler Duty (kW)	2.32	2.16	n/a

The agreement between Pro/II, SpeedUp and the experimental results is generally excellent, especially for the key indicators of bottoms temperature, isobutene conversion and MTBE purity. The most significant discrepancy between the experimental data and the simulation models is the estimate of DIB concentration in the bottoms product. However, both sets of simulation results presented here predict DIB concentrations of around 1% which is also in agreement with previously published simulation results (Abufares and Douglas, 1995), suggesting an alternative explanation for the values reported for the experimental system.

The acceptable accuracy of the MTBE simulations demonstrates the adequacy of the modeling process and validates its extension to ETBE reactive distillation columns where

the column configuration, operating conditions and phase behaviour are similar. Subsequently, there is a high degree of confidence in the ETBE simulation results presented here.

### 3.4 ETBE SIMULATIONS

#### 3.4.1 ETBE Column Simulation Basis

The MTBE laboratory column that was used to validate the reactive distillation model was also used as the basis for the first simulations of an ETBE reactive distillation column. Smith's original column was assumed to contain ten ideal stages: a total condenser, two rectifying stages, one reactive stage, five stripping stages and a partial reboiler. Three reactive stages were specified for the ETBE column so that a higher loading of catalyst was possible to accommodate the lower reaction rate of ETBE compared with MTBE. The feed was specified to consist of a mixture of C<sub>4</sub> hydrocarbons (40% isobutene, 60% 1-butene) and ethanol (at a stoichiometric excess of 5.0%) which had been pre-reacted to 80% isobutene conversion. This mixture was introduced to stage 6 of the column (immediately below the reactive stage). The feed rate and reboiler duty were based on a pilot scale column with an internal diameter of 154 mm. The three available degrees of freedom were satisfied with the following specifications:

- the column pressure was fixed at 950 kPag;
- the reflux ratio was fixed at 5.0;
- the reboiler duty was optimised to maximise the isobutene conversion.

These specifications depart from those used for MTBE in the original catalytic distillation patent application (Smith, 1980). A higher pressure was specified for ETBE to increase the reaction zone temperature and, thereby, improve the reaction rate and reduce the catalyst requirement. A lower reflux ratio was specified to reduce the energy requirements. The original product specification (although not explicitly stated) was clearly unsuitable for ETBE synthesis due to differences in the phase behaviour which affect the product compositions. The complete simulation input is shown in Table 3.4.

Table 3.4 - ETBE Reactive Distillation Column Simulation Input

Feed Specification		Column Specification	
Temperature	30°C	Rectification Stages	2 (inc.condenser)
Rate	0.76 L/min	Reaction Stages	3
Composition (mole basis)	29.1% ETBE, 9.1% ethanol, 7.3% isobutene, 54.5% n-butenes	Stripping Stages	5 (inc.reboiler)
		Total Stages	10
		Overhead Pressure	950 kPa
		Condenser	total
Composition (approx. weight basis)	43.3% ETBE, 6.1% ethanol, 6.0% isobutene, 44.6% n-butenes	Reflux Ratio	5.0
		Reboiler	partial
		Reboiler Duty	8.26 kW
Overall Excess Ethanol	5.0 mol%		

### 3.4.2 ETBE Column Simulation Results

Simulations of this ETBE column were completed using both Pro/II and SpeedUp. The key results are presented in Table 3.5. The estimates of isobutene conversion and ETBE purity differ by less than 1% between the two simulators and the key indicator of bottoms temperature is only 1°C divergent. Figures 3.3 and 3.4 show the column temperature profile and composition profile as predicted by each simulator. Both sets of profiles match well with the only significant discrepancies occurring between estimates of ethanol concentration around the middle of the stripping section and the temperature profile near the top of the column.

The variation in predicted ethanol concentration in the stripping section can be attributed to the difference in vapour phase representation. Although the vapour phase non-ideality is generally low, the fugacity coefficients depart from unity when the ethanol concentration is greater than 10 mol% and can, consequently, produce a significant variation in the K factor (ratio of vapour to liquid concentrations) which affect the composition profiles. The differences in temperature profiles were deemed to be the result of the slightly different vapour pressure correlations that were used: Pro/II used SimSci database constants while published Antoine coefficients were used in the SpeedUp model. The lower isobutene conversion predicted by the SpeedUp model was attributed mostly to the kinetic model of the reaction, which produces a slightly lower isobutene conversion than the equilibrium model which was used in the Pro/II simulations. The overall agreement between the two simulators was excellent and is considered to be an indication of model validity.



Table 3.5 - ETBE Reactive Distillation Column Simulation Results

Property	Pro/II	SpeedUp
Condenser Temperature (°C)	74	79
Reaction Zone Temperatures (°C)	75 - 81	80 - 84
Reboiler Temperature (°C)	159	160
Isobutene Conversion (mol%)	98.3	97.4
Bottoms Composition (wt%)	96.1% ETBE, 2.1% ethanol, 1.7% butenes, 0.06% DIB	96.5% ETBE, 2.8% ethanol, 0.7% butenes, 0.04% DIB
Distillate Composition (wt%)	97.9% n-butenes, 0.9% isobutene, 1.2% ethanol	97.6% n-butenes, 1.7% isobutene, 0.7% ethanol
Condenser Duty (kW)	6.86	6.73
Reboiler Duty (kW)	8.26	8.33
Reaction Rates (mol/min)	0.16 (stage 3), 0.19 (stage 4), 0.15 (stage 5)	0.17 (stage 3), 0.18 (stage 4), 0.12 (stage 5)

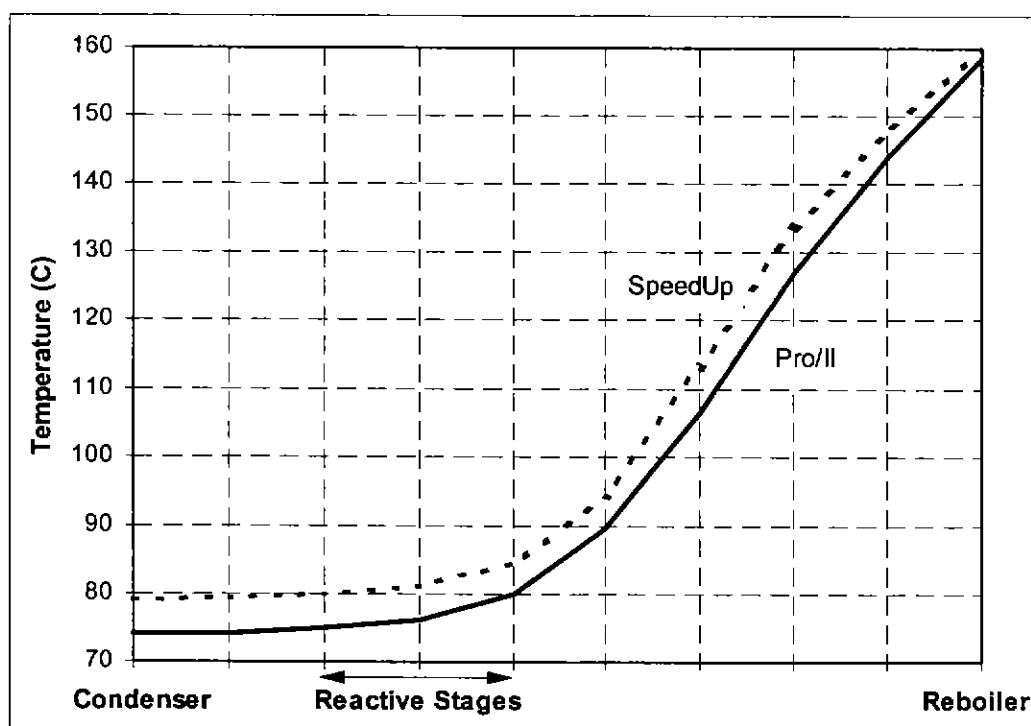


Figure 3.3 - Temperature Profile in the ETBE Column

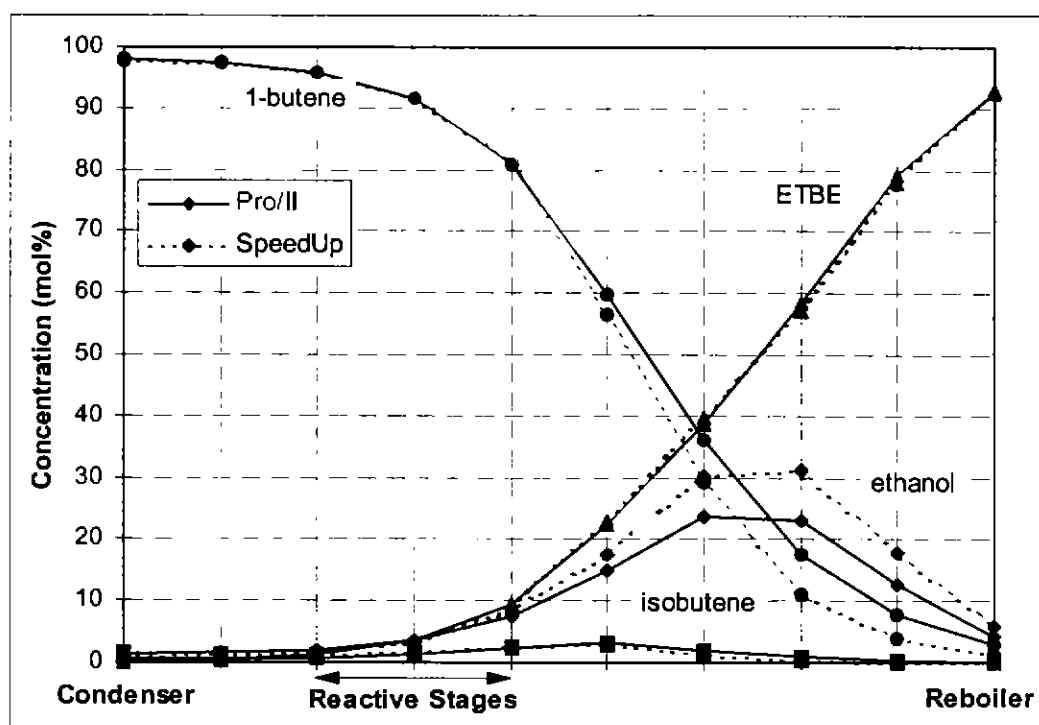


Figure 3.4 - Composition Profiles in the ETBE Column

# CHAPTER FOUR

## DESIGN ISSUES I -

### UNDERSTANDING REACTIVE DISTILLATION

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  - 4.1.1 Introduction
  - 4.1.2 Feed Composition
  - 4.1.3 Stoichiometric Excess of Ethanol
  - 4.1.4 Column Pressure
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  - 4.1.6 Reboiler Duty
  - 4.1.7 Other Operating and Design Variables
- 4.2 Column Topography**
  - 4.2.1 Reactive Section
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    - 4.2.2.3 The Detrimental Effect of Excessive Fractionation
    - 4.2.2.4 MTBE Columns

#### 4.1 OPERATING VARIABLES AND INTERACTIONS

##### 4.1.1 Introduction

Reactive distillation columns behave substantially differently to conventional distillation columns due to interactions between the chemical reaction(s) and vapour-liquid equilibrium. The effects of key design and operating variables are discussed below with reference to two ETBE columns: a column with 10 theoretical stages and the configuration described in Chapter 3; and a column with 30 theoretical stages, based on a commercial MTBE column (Simulation Sciences, 1995). The salient characteristics of these columns are indicated in Table 4.1. Both columns are capable of producing an ETBE product purity and an isobutene conversion in the industrially significant range, although the designs are quite different. Thus, a wide range of operating conditions can be investigated without considered imprudent designs.

In addition to the differences between reactive and non-reactive distillation, there are also substantial differences between ETBE columns and the more common MTBE columns and comparisons are made where relevant. The effects described below should be considered during design and operation of the column to ensure optimal performance.

Table 4.1 - Column Characteristics

	10 Stage Column	30 Stage Column
Rectifying stages (inc. condenser)	2	8
Reactive stages	3	7
Stripping stages (inc. reboiler)	5	15
Feed stage	top stripping stage	top stripping stage
Hydrocarbon feed composition (mol %)	40% isobutene, 60% n-butene	15% isobutene, 85% n-butene
Stoichiometric ethanol excess	5.0 mol%	5.0 mol%
Overhead pressure	950 kPa	600 kPa
Reflux ratio	5.0	1.1

#### 4.1.2 Feed Composition

The hydrocarbon feed composition to an etherification unit is usually fixed by upstream plant operations and varies between 15% and 55% reactive isobutene depending on the type of unit and type of catalyst in use upstream. Standard FCC units produce  $C_4$  streams with 15-20% isobutene while FCC units equipped with new generation catalysts produce  $C_4$  streams with up to 35% isobutene. The  $C_4$  streams from steam cracking and isobutane dehydrogenation units are even richer in isobutene (up to 55%) (Miracca et al., 1996). In each case, the other components are predominantly n-butenes although other  $C_4$ s (mainly isobutane and n-butane) are sometimes also present. Although the operation of the various catalytic and steam cracking units can be varied to increase or decrease isobutene production, other factors (e.g. maximising gasoline production) usually have a more significant economic impact and govern the operation of the unit.

Increasing the concentration of reactive isobutene in the hydrocarbon feed has four main effects on the operation of the reactive distillation column: (a) the energy cost, per kg of ether, decreases as less energy is used in heating and cooling the inert components; (b) the reactant concentrations in the reaction zone increase, with a favourable effect on the reaction equilibrium; (c) the reaction zone temperatures and the reaction zone temperature gradient increase as the stabilising effect of inert components is lessened, with a detrimental effect on the reaction equilibrium; and, (d) the specific reboiler duty must be decreased to maintain optimal reaction conditions, with a detrimental effect on product purity. The overall effect of increasing the isobutene concentration in the feed is usually to decrease the maximum conversion and corresponding ether purity.

The effect of the isobutene feed concentration in ETBE reactive distillation contrasts with MTBE processes where an isobutene concentration of around 60% was found to be optimal for conversion and energy efficiency. A consequence of this result is that, when the isobutene concentration in the hydrocarbon feed is low, ETBE synthesis may be more favourable than MTBE synthesis for some column configurations. However, the presence of significant azeotropes in the MTBE system, between methanol and various butenes, means that isobutene conversion and MTBE product purity can essentially be increased much further by adding stages and/or increasing reflux. This does not necessarily apply to ETBE systems.

The maximum conversion in both the 10 stage and 30 stage columns were determined for varying isobutene concentrations in the hydrocarbon feed to the primary reactor. For all cases, 80% conversion in the reactor was assumed and the reactive distillation reboiler duty was optimised with respect to the final, overall conversion. Table 4.2 shows the maximum final conversions and the corresponding ETBE product purities.

Table 4.2 - Effect of Hydrocarbon Feed Composition on Two ETBE Columns

<b>Isobutene Concentration (mol%)</b>	<b>10 Stage Column</b>		<b>30 Stage Column</b>	
	<b>Maximum Conversion (mol%)</b>	<b>Ether Purity (wt%)</b>	<b>Maximum Conversion (mol%)</b>	<b>Ether Purity (wt%)</b>
15	98.5	95.0	98.7	97.2
20	98.8	96.2	98.6	96.9
30	98.7	96.7	94.5	94.8
40	98.3	96.1	91.7	93.6
50	97.5	95.4	88.5	91.6
60	95.7	94.1	86.6	91.1

ETBE synthesis from pure isobutene and pure ethanol (three component system only) is not feasible as the intersection of phase and chemical equilibrium is not favourable. Too little isobutene is available in the liquid phase for reaction and, at pressures that result in favourable reaction equilibrium, the separation of ethanol and ETBE is difficult. The maximum isobutene conversion and ether purity attainable with a ternary system using the 10 stage column are around 83 mol% and 91 wt%, respectively.

#### 4.1.3 Stoichiometric Excess of Ethanol

The stoichiometric ratio of reactants significantly affects the reaction conversion and the loads on the downstream product purification and reactant recovery equipment. If the reactant excess is too low, product conversion is adversely limited while if it is too high, purification costs are increased and/or product purity is decreased. The choice of percent excess essentially becomes a compromise between operating costs and the value added by the process (a function of market conditions). The control of the stoichiometric ratio is often complicated by the inability to accurately measure feed composition and the need to ensure that global constraints (due to the catalyst, reaction kinetics or other sources) are not violated.

In an MTBE column, the majority of unreacted methanol is recovered in the distillate product via the methanol-butene azeotropes. This places an upper limit on the methanol excess as sufficient butenes must be present in the distillate product to maintain the unreacted methanol below the azeotropic composition (7-12 mol% methanol, depending on the pressure). For example, if the hydrocarbon feed contained 60% isobutene and 40% n-butenes and the azeotropic composition at the operating pressure was 10 mol% methanol, then the maximum methanol excess would be approximately given by:

$$\begin{aligned}
 \text{Unreacted methanol} &\leq 10\% \times (n\text{-butenes} + \text{unreacted isobutene}) \\
 &\leq 10\% \times \text{approximately } 41\% \text{ total hydrocarbon feed} \\
 &\leq 4.1\% \times \text{total hydrocarbon feed} \\
 \text{Reacted methanol} &= \text{reacted iBut} = \text{approximately } 59\% \text{ total hydrocarbon feed} \\
 \text{Maximum methanol excess} &= \frac{4.1\%}{59\%} = 6.9\%
 \end{aligned}$$

Another consequence of recovering methanol overhead via azeotropes is that, below the maximum methanol excess as determined by the feed and azeotropic compositions, increasing the methanol excess has only a limited effect on the bottoms product purity.

However, in an ETBE column, unreacted ethanol is recovered directly with the ether product. This removes any restriction on the ethanol excess but increases the effect the stoichiometric excess has on the ether purity. Therefore, a compromise must be determined between isobutene conversion (which rises as the ethanol excess increases) and ether purity (which falls as the ethanol excess increases). The column configuration influences this decision by changing the relative magnitudes of the two effects but an ethanol excess of 4-7 mol% is considered sufficient to produce a high isobutene conversion without overly

diluting the ether product with ethanol (thereby adding to downstream recovery costs) whilst providing a satisfactory driving force for the reaction. A very high purity ether product can be produced with a lower ethanol excess but some excess should always be used to suppress side reactions involving isobutene. The reaction zone conditions and distillate composition are essentially independent of the stoichiometric excess. Using the 10 stage column configuration as the basis for simulations, Figure 4.1 shows the effect of increasing the ethanol excess on isobutene conversion and ETBE purity.

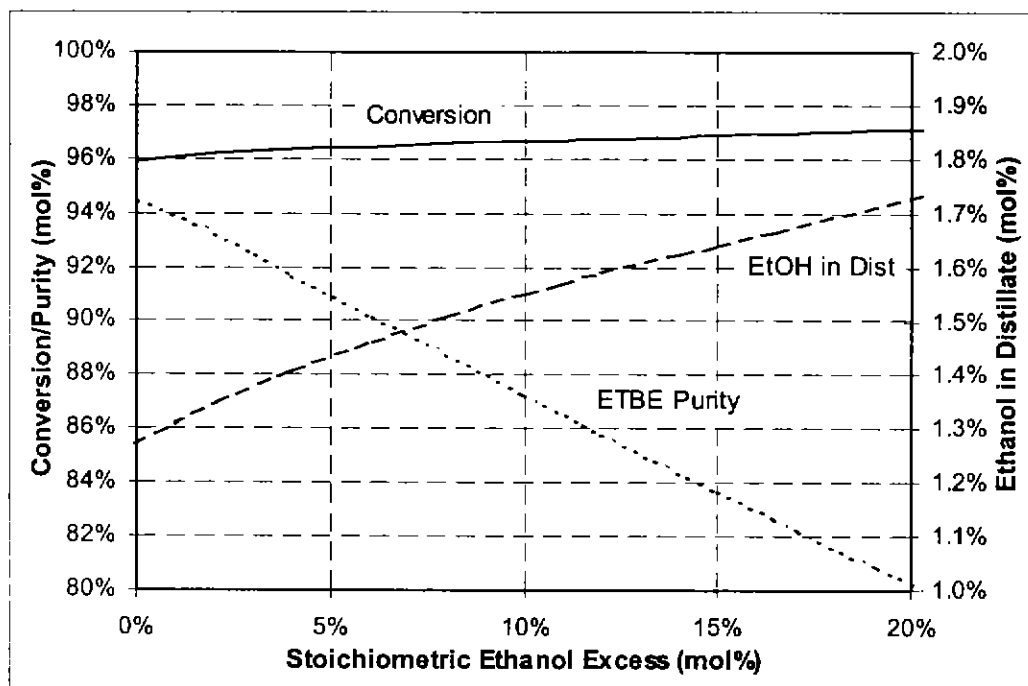


Figure 4.1 - Effects of the Stoichiometric Excess of Ethanol on the 10 Stage ETBE Column

#### 4.1.4 Column Pressure

In conventional distillation, the operating pressure of a column is normally set through an economic rationalisation of heat transfer costs, pumping costs and the value of improved separation. A lower pressure favours separation (due to increasing relative volatility) and reduces the cost of fluid handling and the reboiler while a higher pressure permits cheaper cooling media to be used in the condenser and reduces the heat transfer area required. The optimum design pressure is often the minimum that allows a satisfactory condenser design with either cooling water or air.

The choice of operating pressure in reactive distillation is complicated by the indirect effect of pressure on the reaction equilibrium via changing phase equilibrium temperatures - increasing the pressure raises the reaction zone temperature and decreases the reaction equilibrium constant of exothermic reactions such as ETBE synthesis, thereby lowering conversion. The effect of pressure on the rate constant, via VLE temperature changes, must also be considered, if the reaction is kinetically controlled.

For both ETBE and MTBE systems, the non-ideality of the liquid phase adds two further restrictions to column operations. Firstly, below a certain pressure (about 130 kPa for ETBE and 300 kPa for MTBE columns) the highest boiling component is the alcohol rather than the ether. Operating below this pressure will drive the ether product back to the reaction zone and will result in low conversion and low ether purity. Secondly, the overhead pressure affects the composition (and presence) of the alcohol-butene azeotropes.

The range of effects that need to be considered in selecting the column operating pressure suggest that an accurate simulation is almost essential for reactive distillation column design. Table 4.3 shows the maximum conversion attainable (and the corresponding reaction zone temperatures and ether purity) in the two ETBE columns that are described in Table 4.1 for various values of the overhead pressure. The column pressure profile (i.e. the total pressure drop across the trays or packings) was fixed for each case and chemical equilibrium was assumed on each reactive stage at all pressures. With these assumptions, the optimum overhead pressure with respect to conversion was found to be 400-500 kPa. However, a higher pressure might be required in practice as the reaction equilibrium becomes less likely (or requires more catalyst) at lower pressures due to kinetic limitations. The optimum operating pressure with respect to conversion was found to be slightly higher in the 30 stage column. Interestingly, the effect of pressure on the ether purity (at the maximum conversion) was directionally opposite in two columns. Indeed, a much higher operating pressure could be preferred in a taller column in order to achieve a very high ETBE product purity (e.g. greater than 99.9 wt%).

This data shows that the choice of an operating pressure depends on many factors and the recommendation of a single 'optimum' operating pressure for ETBE columns is not appropriate. However, the variability in the data suggests that it is appropriate to undertake an optimisation of the operating pressure for a given set of site factors that include the feed composition, local production constraints and product specifications. Operating pressures of commercial columns could (and probably should) vary substantially from site to site. However, as a rule-of-thumb, it is considered that a column pressure such that the reaction



zone temperatures are 5-15°C lower than those used in the pre-reactor should guarantee high conversion, high ether product purity and manageable reaction rates.

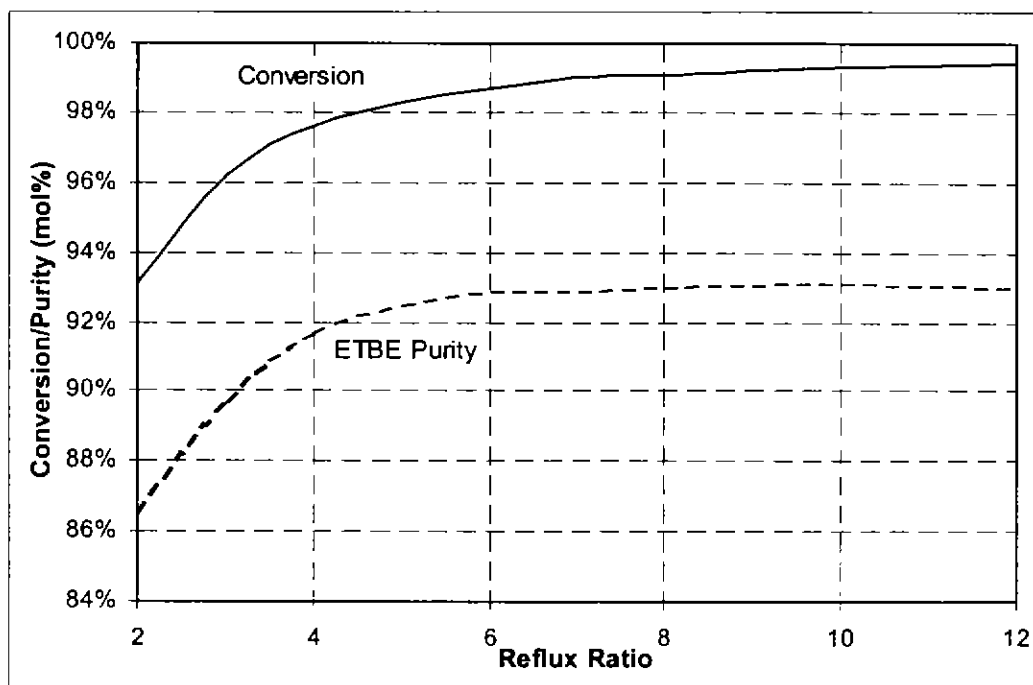
Table 4.3 - Effect of Column Overhead Pressure on the ETBE Columns

Overhead Pressure (kPa)	10 Stage Column			30 Stage Column		
	Reaction Zone Temp (°C)	Maximum Conversion (mol%)	Ether Purity (wt%)	Reaction Zone Temp (°C)	Maximum Conversion (mol%)	Ether Purity (wt%)
400	44-53	99.0	97.0	44-50	99.1	97.1
500	51-59	99.2	97.1	51-56	98.9	97.1
600	57-65	99.1	97.1	57-62	98.7	97.3
700	63-70	99.0	97.0	62-67	98.6	97.6
800	68-74	98.8	96.6	67-72	98.6	98.1
900	72-79	98.5	96.4	72-77	98.2	98.3
1000	77-82	98.2	95.9	77-81	98.0	99.1
1100	81-86	97.8	95.3	81-85	97.7	99.9

#### 4.1.6 Reflux Ratio

Reflux has a dual purpose in reactive distillation. Increasing reflux rate enhances separation and recycles unreacted reactants to the reaction zone and, thereby, increases conversion. Several effects occur as a result of increasing the reflux ratio: (a) the concentrations of reactants in the distillate are reduced; (b) the reaction zone temperatures are reduced; and (c) the concentration of ether in the reaction zone is reduced. Each of these effects contributes to the increased conversion. Figure 4.2 indicates the relationship between reflux ratio and isobutene conversion for the 10 stage column only. Although the conversion increases monotonically with reflux ratio, the ether purity remains approximately constant for all ratios greater than 6 due to the increasing load on the stripping section as the amount of ETBE in the column increases.

High reflux ratios add to energy requirements and increase the minimum size of all components in the distillation system. Consequently, reflux and stages are often traded against each other in conventional distillation design in order to minimise the total cost of the process. However, it is not always possible to duplicate the effects of reflux with additional separation stages in reactive distillation as only the separation effects are recreated (i.e. the benefits of recycling components to the reaction zone are lost). This is particularly true for ETBE columns and a relatively high reflux ratio is favoured.



**Figure 4.2 - Effect of Reflux Ratio on the 10 Stage ETBE Column**

#### **4.1.7 Reboiler Duty**

The reboiler duty is one of the principal points of control in a distillation column. In normal distillation, there is a monotonic, albeit sometimes highly non-linear, relationship between the reboiler duty and the principal operating objective (Kister, 1992). In reactive distillation, the reboiler duty must be set to ensure sufficient recycle of unreacted, heavy reactant to the reaction zone without excluding the light reactant from the reaction zone. If the reboiler duty is too high or too low, conversion, and subsequently product purity, is reduced. Figure 4.3 indicates the effect of reboiler duty on conversion and ether purity in the 10 stage ETBE column and clearly shows the presence of an optimum duty. There is only a narrow range of duties that produce an ether purity above 90%. Consequently, tight control is required to achieve acceptable operation.

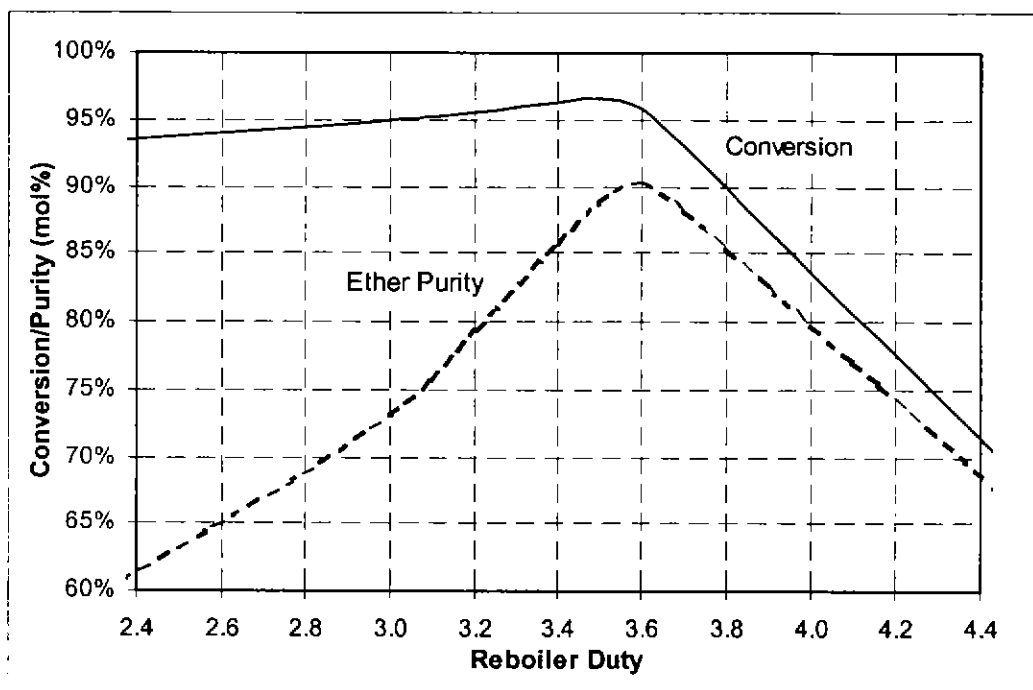


Figure 4.3 - Effect of Reboiler Duty on the 10 Stage ETBE Column

#### 4.1.8 Other Operating and Design Variables

The extent of reaction performed prior to the reactive distillation column should simply be an economic optimisation between the relative costs of the two operations. Initially, it is easy to produce ether in a simple tubular reactor with some form of temperature control to prevent the exothermicity of the reaction from heating the reactor contents and, eventually, stopping the reaction due to equilibrium considerations. However, at higher conversions, very low reaction temperatures are required with a subsequent high demand for catalyst due to the low reaction rates. Under these conditions, reactive distillation becomes more economical.

The optimum feed point to the reactive distillation column is just below the reactive section to avoid ETBE decomposition which can result with the relatively ETBE rich product from the reactor. Feeding too far below the reactive section reduces the stripping potential of the column and increases the energy required for separation. Split feeding to each of the reactive stages is possible but creates a high concentration of ETBE at the top of the reactive section (leading to decomposition towards the bottom of the reactive section) and, again, increases the energy required for separation.

The feed temperature has only a very slight effect on the operation of either an ETBE or MTBE reactive distillation column. A cooler feed has a mildly beneficial effect on the reaction zone temperature but this can be offset by a shift in phase equilibrium. To

minimise equipment requirements the feed should be supplied at its process temperature, which is likely to be close to the reactor temperature (70-90°C). If intermediate storage is required for any reason, an ambient feed is also acceptable. Neither feed heaters nor feed coolers are required for a satisfactory process design.

## 4.2 COLUMN TOPOGRAPHY

### 4.2.1 Reactive Section

The function of the reactive section of the column is simply to provide a site for the main reaction to proceed and, as such, there is no particular requirement for separation. This suggests that only one equilibrium stage of a column needs to be packed with catalyst although the physical size of this stage could be quite large to meet the catalyst requirement. However, simulations show that higher conversions are possible where more than one equilibrium stage is reactive. Figure 4.4 shows the effect of varying the number of reactive stages in the 10 stage ETBE column described in Table 4.1. All other variables, including the number of separation stages, reflux ratio, reboiler duty and feed conditions were fixed.

The improved conversion with an increased number of reactive stages results from the benefits of the additional separation which are gained. Under most conditions, transferring all the catalyst in a column to a single stage would have a negligible effect on the overall conversion achieved. Note that this is different to the data presented in Figure 4.4 as it implies an increase in the number of separation stages at the expense of reactive stages.

Increasing the number of reactive stages above the optimum (four for this column) produced a detrimental interaction between the phase and chemical equilibrium which led to the decomposition of product on the lower reactive stages. This is to be expected as the increased fractionation that occurs with more stages concentrates the ether in the lower reactive stages and shifts the chemical equilibrium back to the reactants. An excessive number of reactive stages can also encourage unwanted side-reactions and increase the concentration of impurities in the ether product. By comparison, the MTBE simulations showed no optimum although the benefits of adding a reactive stage became progressively smaller when high numbers of reactive stages were already present, due to the increased likelihood of decomposition on the lower reactive stages.

Supplying catalyst on several reactive stages allows the total catalyst loading in the column to be increased and may, therefore, extend the time between catalyst changes or regenerations. However, during the life of the catalyst the main reaction site may shift

within the column and change the effective number of rectification and stripping stages and, subsequently, change the conversion and purity attained.

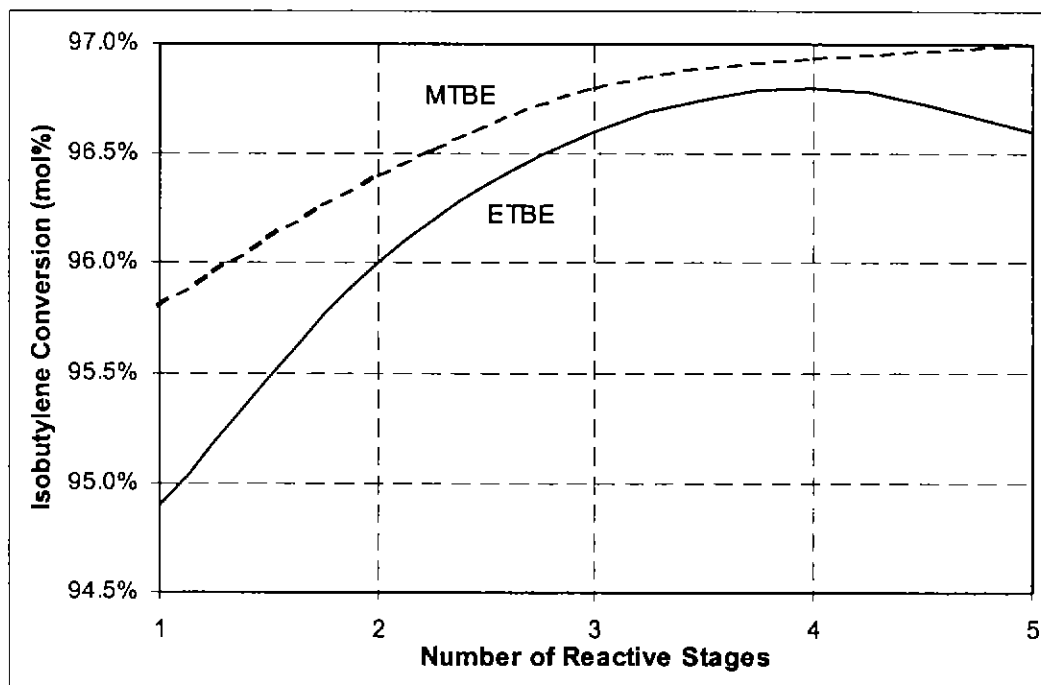


Figure 4.4 - Effect of Additional Reactive Stages in the 10 Stage ETBE Column

#### 4.2.2 Non-Reactive Sections

##### 4.2.2.1 Interaction Between Fractionation and Feed Composition

The non-reactive sections of a hybrid reactive distillation column are vital to achieving the desired process performance. Ideally, the rectification section of a reactive distillation column for ether synthesis should: (a) remove light inerts from the reaction zone; (b) prevent loss of ether or alcohol in the distillate; and, (c) recycle unreacted reactants (olefin and alcohol) to the reaction zone. For an ETBE column, this would ideally require a separation between isobutene and the heaviest non-reactive hydrocarbon lighter than isobutene. In practice, this is almost impossible to achieve whilst maintaining acceptable reaction zone conditions. However, the loss of ether in the distillate can be minimised without rejecting isobutene from the column. More rectification stages are required to also prevent loss of ethanol with the distillate.

The stripping section should, ideally: (a) remove ether from the reaction zone to maintain favourable reaction conditions; (b) purify the ether product; (c) prevent loss of reactive olefin with the ether product; and (d), minimise ethanol loss with the ether product. In an ETBE column, this implies a separation between ethanol and ETBE, which is largely achievable at the conditions of temperature and pressure required for adequate reaction.

Manipulating the number of stripping stages provides a mechanism for controlling the volatility, flash point and composition of the ether product.

Although the separation objectives are clear, changes in the separation efficiency within a multicomponent system tend to adjust composition profiles rather than produce more clearly defined product splits when intermediate boiling components (e.g. ethanol) are involved. Consequently, an increase in rectification or stripping separation is not necessarily beneficial for reaction zone conditions. Too much rectification separation can result in isobutene loss via the distillate. Too much stripping separation can result in ethanol being drawn away from the reaction zone and concentrated just above the reboiler. For some processes, including ETBE, both the rectification and stripping separation must be optimised. Figures 4.5 and 4.6 present data based on the 10 stage ETBE column and both graphs include distinct optimums.

The ratio between the number of rectification and stripping stages and the feed composition are also important factors that should be considered. If the rectification separation is too great without light inerts present to stabilise the reaction conditions, then reboiler operation must be adjusted to compensate the reaction conditions resulting in a loss of ether purity. Tables 4.4 and 4.5 show this effect for two different feed compositions: a low isobutene feed with 15% isobutene in the hydrocarbon to the primary reactor; and, a high isobutene feed derived from a 50/50 mixture of isobutene and n-butenes. The number of reactive stages and the reflux ratio were kept constant for all simulations and the reboiler duty was optimised with respect to the conversion in each case. The combination of two rectification stage and 16 stripping stages produced the best results in each case. Adding rectification stages is beneficial with only a few stripping stages present but detrimental with many. With a high concentration of isobutene in the hydrocarbon feed, the magnitudes of all the effects are diminished and the need to optimise (rather than maximise) separation becomes apparent.

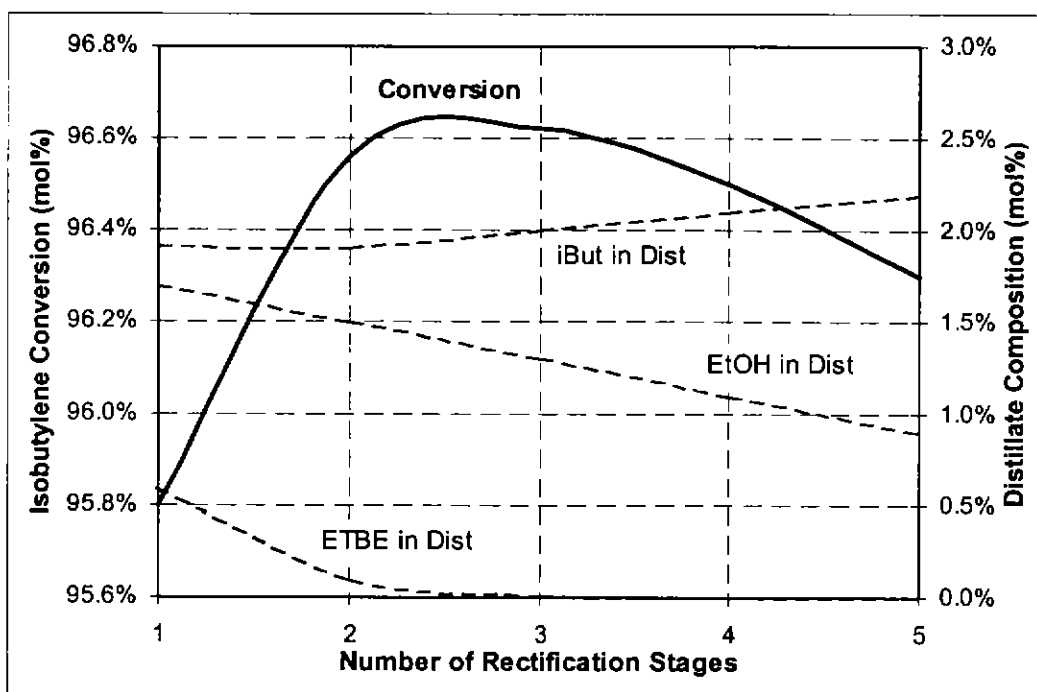


Figure 4.5 - Effect of Rectification Separation

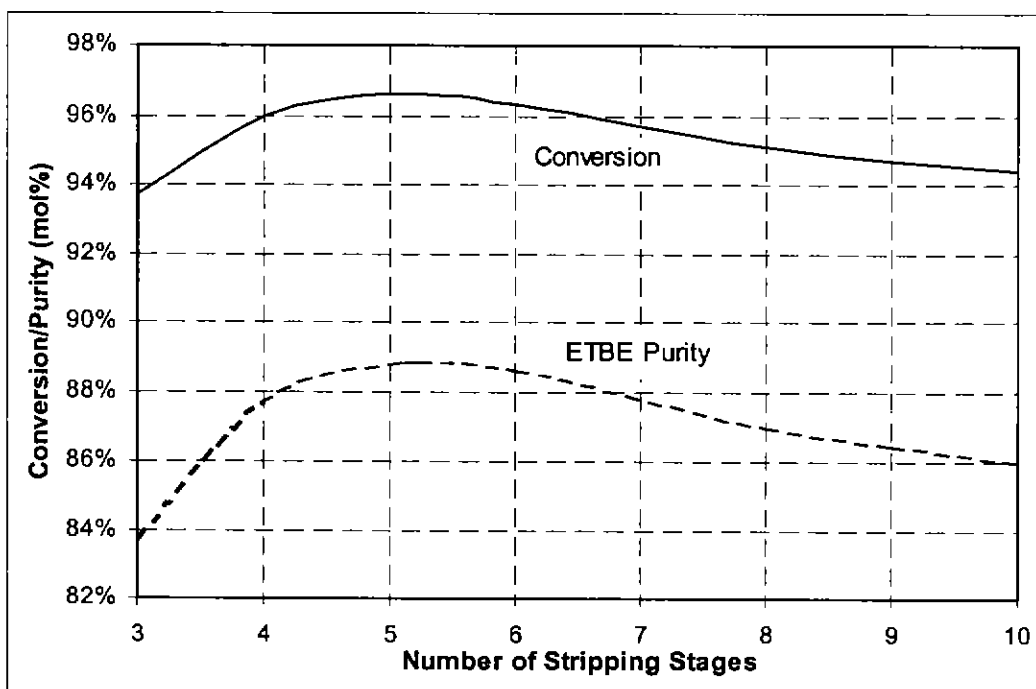


Figure 4.6 - Effect of Stripping Separation

Table 4.4 - Effect of Separation Stages on ETBE Columns with Lean Isobutene Feeds

Rectification Stages	Stripping Stages		
	4	8	16
2	98.6 mol% conversion; 90.3 wt% purity (8.8 wt% butenes)	99.4 mol% conversion; 99.7 wt% purity (0.21 wt% butenes)	99.4 mol% conversion; 99.95 wt% purity (~0 wt% butenes)
4	98.8 mol% conversion; 92.2 wt% purity (6.8 wt% butenes)	99.5 mol% conversion; 99.2 wt% purity (0.17 wt% butenes)	99.5 mol% conversion; 99.7 wt% purity (~0 wt% butenes)
8	99.0 mol% conversion; 98.6 wt% purity (0.16 wt% butenes)	99.5 mol% conversion; 98.6 wt% purity (0.16 wt% butenes)	99.5 mol% conversion; 98.9 wt% purity (~0 wt% butenes)

Table 4.5 - Effect of Separation Stages on ETBE Columns with Rich Isobutene Feeds

Rectification Stages	Stripping Stages		
	4	8	16
2	97.3 mol% conversion; 93.1 wt% purity (6.6 wt% butenes)	97.8 mol% conversion; 97.0 wt% purity (0.05 wt% butenes)	98.2 mol% conversion; 97.2 wt% purity (~0 wt% butenes)
4	97.2 mol% conversion; 93.2 wt% purity (3.6 wt% butenes)	98.2 mol% conversion; 97.0 wt% purity (0.08 wt% butenes)	98.2 mol% conversion; 97.1 wt% purity (~0 wt% butenes)
8	97.1 mol% conversion; 93.2 wt% purity (3.5 wt% butenes)	98.0 mol% conversion; 96.7 wt% purity (0.14 wt% butenes)	98.2 mol% conversion; 97.1 wt% purity (~0 wt% butenes)

#### 4.2.2.2 Optimising Fractionation

The optimal column topography depends on the operating objectives (e.g. maximum isobutene conversion, minimum ethanol in the ETBE product, etc.), the vapour-liquid loading and the feed composition. The simulation results presented above suggest that



additional fractionation stages are sometimes detrimental but their effect is dependent on the column conditions. In order to investigate this phenomenon further, a series of column designs were completed for an isobutene-rich feed and an isobutene-lean feed.

The isobutene-rich feed was modelled on the product of a typical steam cracker and was specified to comprise 30 mol% isobutene, 40% n-butenes and 30% butadiene. The isobutene-lean feed was based on a typical catalytic cracker product containing 15 mol% isobutene, 35% n-butenes, 40% isobutane and 10% n-butane. Using a consistent design philosophy, the total number of stages and the reflux ratio were varied to determine the optimal column topography for each feed. The design basis was:

- equilibrium stages allocated in the ratio of one rectifying stage to one reactive stage to two stripping stages;
- feed to the uppermost stripping stage;
- overhead pressure fixed at 700 kPa;
- base case reflux ratio of 1.2 for the isobutene-rich feed and 0.8 for the isobutene-lean feed (selected to reflect the increased distillate rate which results from the presence of more  $C_4$  inerts in the isobutene-lean feed);
- a bottoms product composition specification of 0.1 wt% total  $C_4$ s (selected to produce a low product RVP without overly constraining the column operation).

The total number of stages was varied from 6 (condenser, 1 rectifying stage, 1 reactive stage, two stripping stages and reboiler) to 42 (condenser, 10 rectifying stages, 10 reactive stages, 20 stripping stages and reboiler), and the reflux ratio was varied up to a maximum of 50% more than the base case.

Five designs for each feed composition are shown in Tables 4.6 and 4.7. The highest values of isobutene conversion and ETBE purity were achieved with relatively few theoretical stages and a high reflux ratio for both feed compositions (Design D). However, Design C would probably be preferred for isobutene-rich feed because it results in a distillate product that is relatively free of ethanol and ETBE. With an isobutene-lean feed, the benefit of restricting the number of stages and maximising the reflux ratio (i.e. Design D) is more pronounced and should easily compensate for the reduced distillate purity.

Table 4.6 - ETBE Reactive Distillation Column Designs (Isobutene-Rich Feed)

	Design A	Design B	Design C	Design D	Design E
Number of theoretical stages (rectifying/reactive/stripping)	7 / 7 / 14	7 / 7 / 14	4 / 4 / 8	3 / 3 / 6	2 / 2 / 4
Reflux ratio	1.2	1.8	1.8	1.8	1.8
Reboiler duty relative to Design A	1.00	1.25	1.23	1.25	1.77
Overall isobutene conversion	88.8%	89.5%	91.7%	92.6%	60.7%
Bottoms composition (wt%)	91.3% ETBE, 7.5% EtOH, 1.1% DIB, 0.1% C <sub>4</sub> s	91.2% ETBE, 7.1% EtOH, 1.6% DIB, 0.1% C <sub>4</sub> s	92.8% ETBE, 6.1% EtOH, 1.0% DIB, 0.1% C <sub>4</sub> s	94.0% ETBE, 5.4% EtOH, 0.5% DIB, 0.1% C <sub>4</sub> s	78.4% ETBE, 21.0% EtOH, 0.4% DIB, 0.1% C <sub>4</sub> s
Distillate composition (wt%)	6.0% iBut, 94.0% other C <sub>4</sub> s, 3 ppm EtOH	4.9% iBut, 95.1% other C <sub>4</sub> s, 1 ppm EtOH	4.2% iBut, 95.8% other C <sub>4</sub> s, 100 ppm EtOH, 20 ppm ETBE	4.2% iBut, 95.4% other C <sub>4</sub> s, 0.4% EtOH, 100 ppm ETBE	19.5% iBut, 76.5% other C <sub>4</sub> s, 3.0% EtOH, 1.0% ETBE

Table 4.7 - ETBE Reactive Distillation Column Designs (Isobutene-Lean Feed)

	Design A	Design B	Design C	Design D	Design E
Number of theoretical stages (rectifying/reactive/stripping)	7 / 7 / 14	7 / 7 / 14	4 / 4 / 8	3 / 3 / 6	2 / 2 / 4
Reflux ratio	0.8	1.2	1.2	1.2	1.2
Reboiler duty relative to Design A	1.00	1.25	1.25	1.27	1.41
Overall isobutene conversion	91.6%	92.8%	94.0%	97.1%	75.7%
Bottoms composition (wt%)	92.8% ETBE, 6.0% EtOH, 0.9% DIB, 0.1% C <sub>4</sub> s	93.2% ETBE, 5.5% EtOH, 1.0% DIB, 0.1% C <sub>4</sub> s	94.3% ETBE, 4.6% EtOH, 0.9% DIB, 0.1% C <sub>4</sub> s	97.8% ETBE, 1.3% EtOH, 0.7% DIB, 0.1% C <sub>4</sub> s	92.7% ETBE, 6.6% EtOH, 0.5% DIB, 0.1% C <sub>4</sub> s
Distillate composition (wt%)	1.1% iBut, 98.7% other C <sub>4</sub> s, 0.2% EtOH	0.9% iBut, 99.0% other C <sub>4</sub> s, 0.1% EtOH	0.7% iBut, 99.1% other C <sub>4</sub> s, 0.2% EtOH, 2 ppm ETBE	0.3% iBut, 99.0% other C <sub>4</sub> s, 0.7% EtOH, 20 ppm ETBE	3.7% iBut, 93.8% other C <sub>4</sub> s, 2.2% EtOH, 0.3% ETBE

The directional effects of both reflux and fractionation were consistent with earlier observations: increasing the reflux ratio was found to be universally beneficial but excessive fractionation was detrimental to the isobutene conversion and the ether purity. However, additional separation stages always produce a purer distillate product which contained less ethanol and ETBE. This is potentially significant if there is no ethanol recovery equipment downstream of the reactive distillation column (possible for ETBE production since the ethanol concentration in the distillate is typically very low) and ethanol is an unwanted contaminant or poison in a downstream process, and might be a sufficient justification for specifying a column with more than the optimal number of separation stages. Although the trade-off between reflux and stages can be employed to control the distillate purity, it is not possible to match the process performance (i.e. conversion and ether purity) from the optimal topography with a taller column regardless of the combination of reflux ratio and column specifications that might be used.

#### *4.2.2.3 The Detrimental Effect of Excessive Fractionation in Reactive Distillation*

To confirm the apparent result that fractionation can be detrimental in the design of reactive distillation columns, a third series of designs were completed to compare reactive and non-reactive distillation. A hydrocarbon stream containing 25% isobutene and 75% n-butene was combined with a stoichiometric amount of ethanol and reacted to 75% isobutene conversion in order to create a suitable feed for a series of reactive and non-reactive columns with varying numbers of stages. The same distribution of stages (i.e. constant ratio of rectifying : reactive : stripping stages), product specification (i.e. 0.1%  $C_4$  in the bottoms) and reboiler duty were specified in each column. The non-reactive column was identical to the reactive column with the reactive stages exchanged for non-reactive stages.

The intuitive effect of increasing fractionation with a constant composition specification is to increase the yield of the product under control. In this case, the bottoms rate should increase with the number of stages in the column. This behaviour is seen exactly in the non-reactive column. This is shown in Figure 4.6 for two values of the reboiler duty (0.95 and 2.50 MW per 100 kmol/hr of  $C_4$  feed).

The reactive columns produced a completely different response and the bottoms product yield was maximised at an intermediate number of separation stages. This is shown in Figure 4.7 which describes the same cases as Figure 4.6. Figure 4.8 shows how the ETBE purity and the isobutene conversion vary with the total number of stages in the reactive column. As indicated previously, the interaction between the phase and reaction equilibrium is such that the isobutene conversion (and, hence, also the ETBE purity) is

maximised when the column internal compositions are optimised. This occurs at an intermediate level of fractionation rather than an extreme.

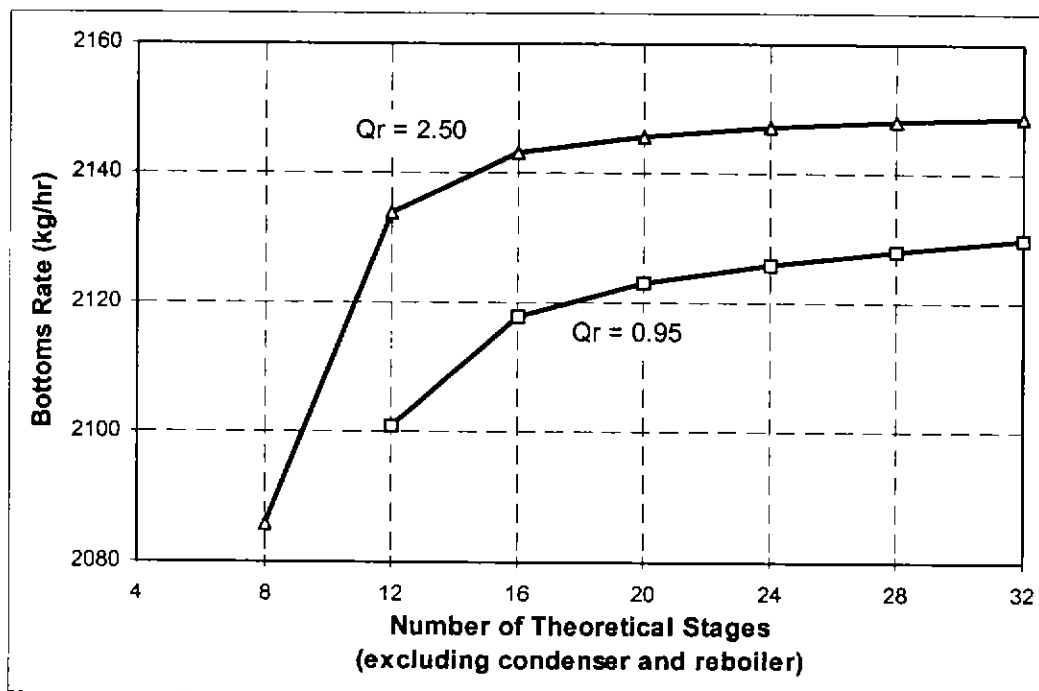


Figure 4.6 - Effect of Fractionation in Non-Reactive ETBE Distillation

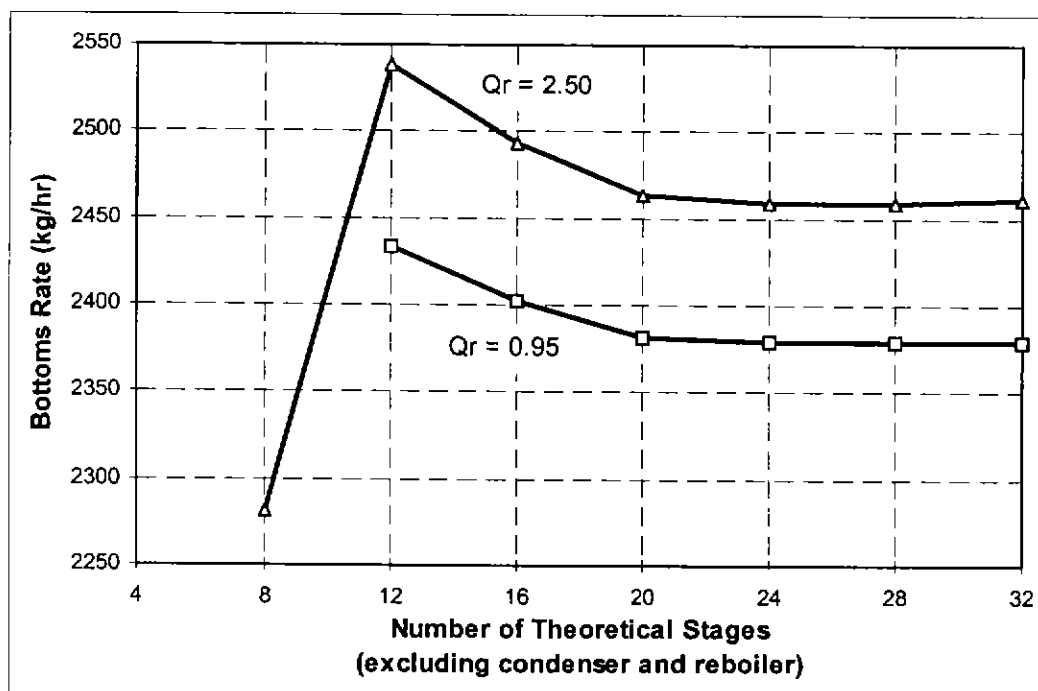


Figure 4.7 - Effect of Fractionation in Reactive ETBE Distillation

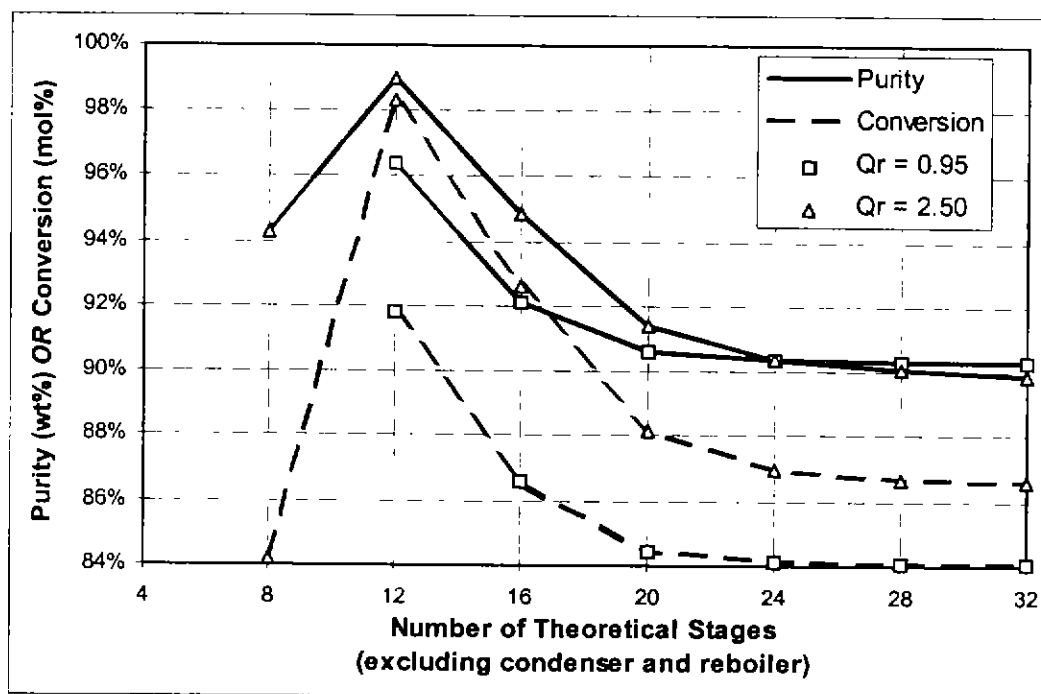


Figure 4.8 - Effect of Fractionation on ETBE Purity and Conversion

#### 4.2.2.4 MTBE Columns

The effect of fractionation on MTBE columns was considered by repeating the above analyses with methanol in the feed. Interestingly, somewhat different results were observed. The benefit of increasing the reflux ratio was still evident (the predominant effect of this is to recycle reactive components) but no advantage was found from reducing the fractionation from the base case of 30 ideal stages. The different behaviour is again caused by the methanol- $C_4$  azeotropes. Provided the internal ratio of methanol to  $C_4$  is lower than the azeotropic composition, the effect of increasing the stripping section separation is to recycle methanol to the reactive section and promote further reaction. Unfortunately, a similarly useful azeotrope does not exist at the top of the column so that the rectifying separation must again be optimised. In fact, as with the ETBE system, the reactive distillation of MTBE is infeasible with perfect separation (infinite stages and infinite reflux).

## CHAPTER FIVE

### DESIGN ISSUES II - DESIGN METHODS

- 5.1 Feasibility of a Reaction-Separation**
  - 5.1.1 Distillation Residue Curves
    - 5.1.1.1 Governing Equations*
    - 5.1.1.2 ETBE System*
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    - 5.1.1.4 Significance for Reactive Distillation Column Design*
  - 5.1.2 Reactive Residue Curves
    - 5.1.2.1 Governing Equations*
    - 5.1.2.2 ETBE System*
    - 5.1.2.3 MTBE System*
    - 5.1.2.4 Kinetically Controlled Reactions*
    - 5.1.2.5 Significance for Reactive Distillation Column Design*
  - 5.1.3 Hybrid Residue Curves
- 5.2 Proposed Design Strategy for Hybrid Reactive Distillation**

### 5.1 FEASIBILITY OF A REACTION-SEPARATION

#### 5.1.1 Distillation Residue Curves

##### *5.1.1.1 Governing Equations*

Residue curves describe the composition profiles that result when a mixture is subject to simple batch distillation as shown in Figure 5.1. The liquid composition changes as the more volatile components of the mixture are removed preferentially. Eventually, the composition of the residue approaches a stable node that is either a non-volatile pure component or a high-boiling azeotrope.

The equations governing this process are the material balances (equations 5.1 and 5.2), the energy balance (equation 5.3) which can be simplified at bubble point by assuming that the temperature is a function of the composition only (effectively equation 5.4) and phase equilibrium (equations 5.5 and 5.6):

$$\frac{dM}{dt} = -V \quad (5.1)$$

$$\frac{d(Mx_i)}{dt} = -Vy_i \quad (5.2)$$

$$\frac{d(MH)}{dt} = Q - VH^v \quad (5.3)$$

$$\frac{dH}{dt} = 0 \quad (5.4)$$

$$P \cdot y_i = \gamma_i \cdot x_i \cdot P_i^{vap} \quad (5.5)$$

$$\sum y_i = 1 \quad (5.6)$$

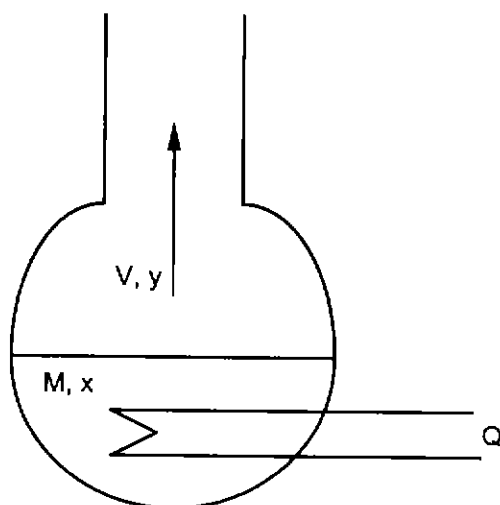


Figure 5.1 - Simple Distillation Process

The physical properties (activities, enthalpies and vapour pressures) can be calculated by any appropriate method. The UNIFAC model, Soave-Redlich-Kwong equations and published Antoine coefficients are recommended for the ETBE system (and the MTBE system). The steady state solution of these equations is of no significance but the transient solutions form residue curves. The required boundary conditions are pressure ( $P$ ), initial volume ( $M_0$ ), initial composition ( $x_0$ ), and the heating rate ( $Q$ ) but only the pressure and initial composition affect the residue curve trajectory. The ratio of  $Q$  to  $M$  determines the boiling rate and, therefore, the sampling time required to obtain a curve with good resolution.

The residue curves are not unique for a given combination of pressure and composition as any point on the residue trajectory can be used as the initial point for that curve. Reversing the sign of equations (5.1)-(5.3) allows residue curves to be constructed towards an unstable node (volatile pure component or low-boiling azeotrope).



### 5.1.1.2 ETBE System

Figures 5.2-5.4 show families of residue curves for the quaternary system of ethanol-isobutene-ETBE-(n-butene). Isobutene and n-butene have been lumped together for clearer visualisation. Three different operating pressures were considered: atmospheric pressure (Figure 5.2), 950 kPag (Figure 5.3) and 1500 kPag (Figure 5.4). The three diagrams only differ with respect to the location of the ethanol-ETBE azeotrope although the curvature of the residue trajectories near the ETBE-C<sub>4</sub> border also varies somewhat.

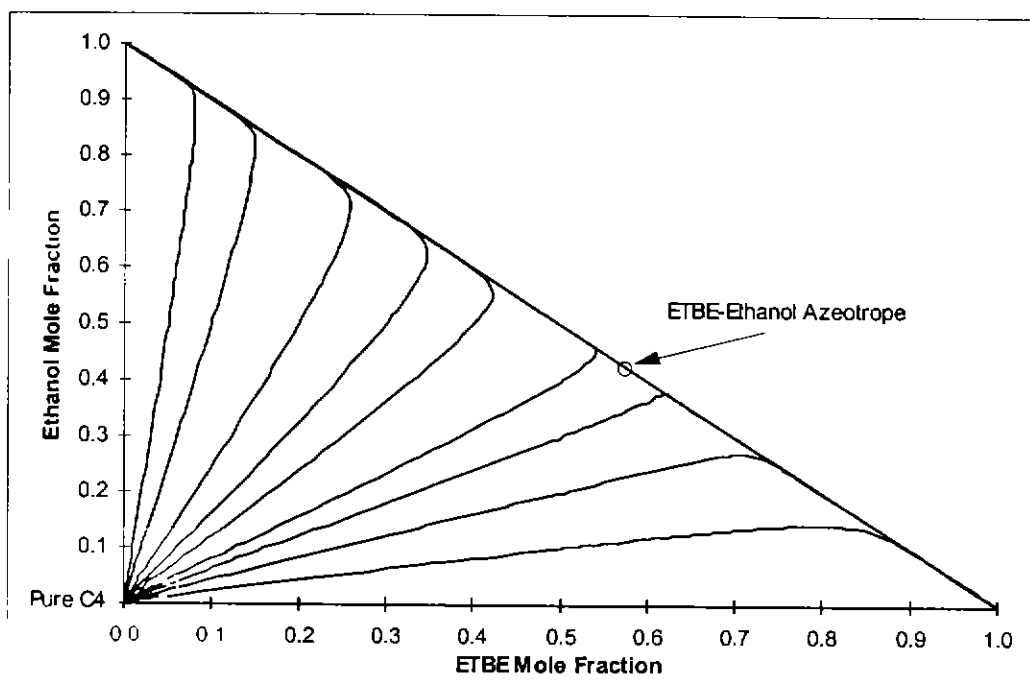


Figure 5.2 - Residue Curve Diagram for the ETBE System at Atmospheric Pressure

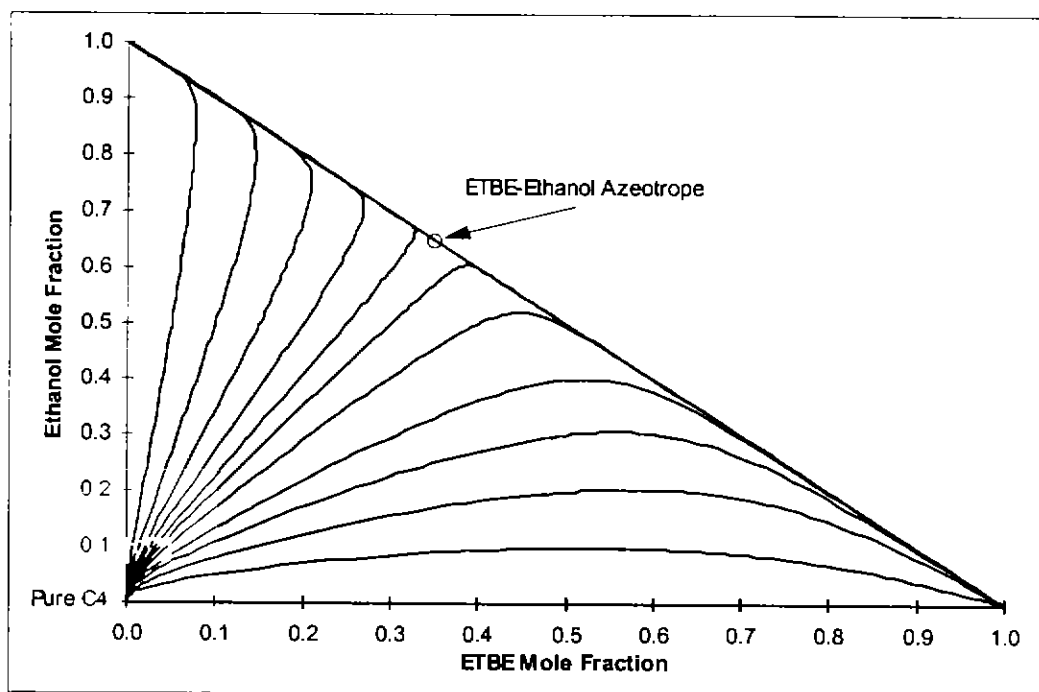


Figure 5.3 - Residue Curve Diagram for the ETBE System at 950 kPag

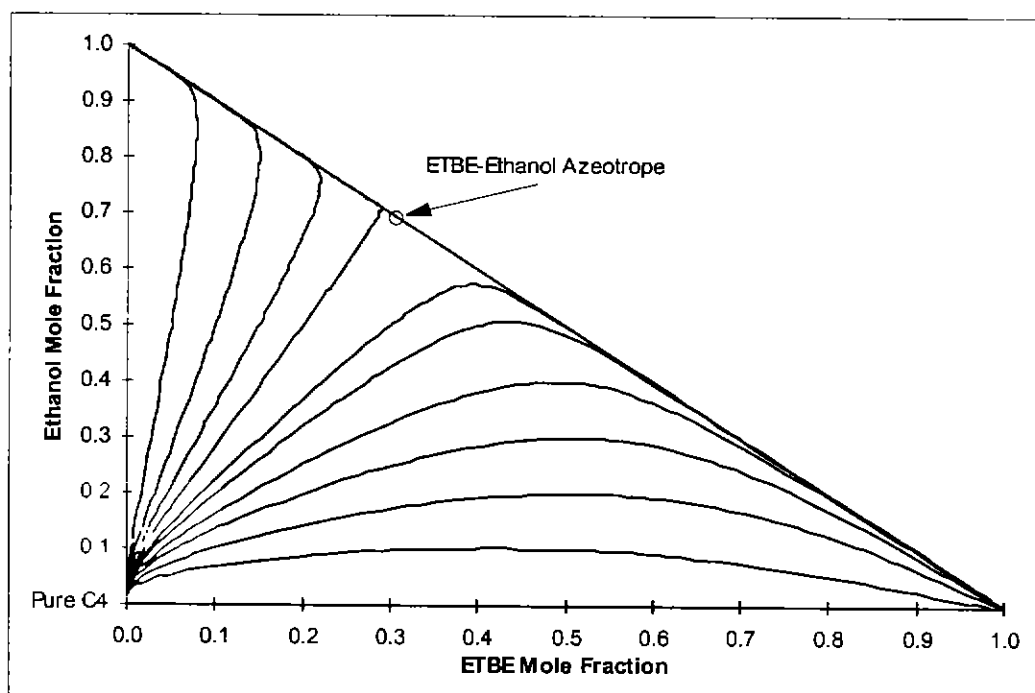


Figure 5.4 - Residue Curve Diagram for the ETBE System at 1500 kPag

#### 5.1.1.3 MTBE System

Residue trajectories for the MTBE system are shown in Figure 5.5 for comparison with the ETBE system. A ternary system consisting only of methanol, MTBE and n-butene was used to construct the diagram to highlight the azeotrope between methanol and n-butene. In practice, this azeotrope only acts as a pinch point as there is no azeotrope between methanol

and isobutene. Pure  $C_4$  is a feasible distillate composition, but only in a column which approaches perfect fractionation (infinite stages and infinite reflux ratio, or the  $\infty/\infty$  case).

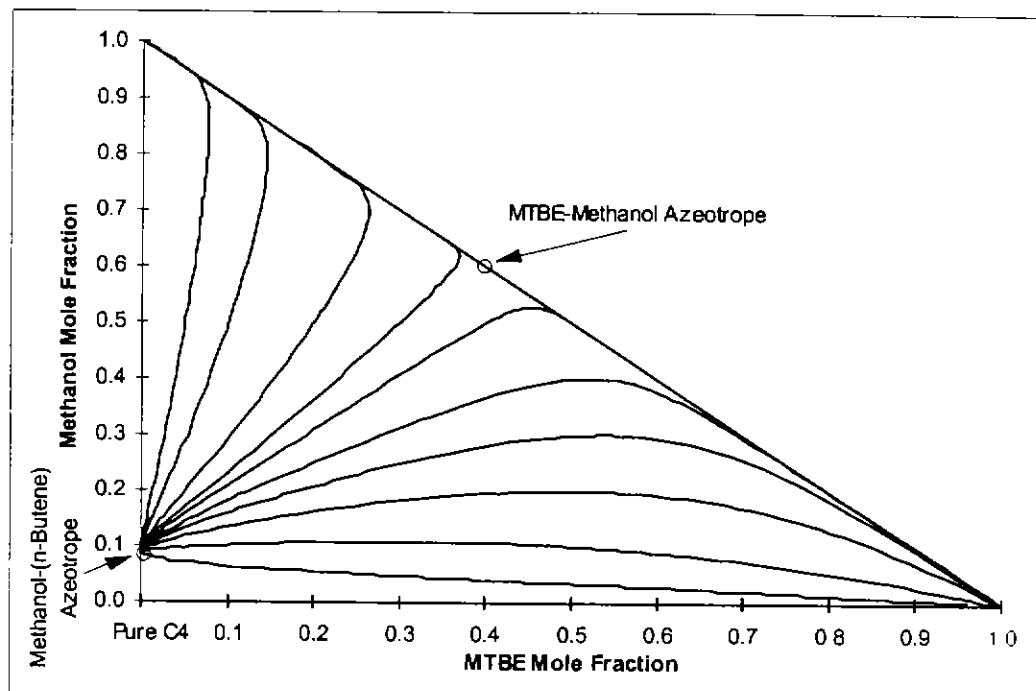


Figure 5.5 - Residue Curve Diagram for the MTBE System at 950 kPag

#### 5.1.1.4 Significance for Reactive Distillation Column Design

Although residue curves are based on a batch distillation process, the trajectory of each curve corresponds closely to the composition profile which is seen in a column with perfect fractionation (i.e. the  $\infty/\infty$  case). Residue curve diagrams also define distillation regions and boundaries that cannot be crossed by simple distillation. These boundaries extend from the ethanol-ETBE azeotrope to the  $C_4$  node in the ETBE system (Figures 5.2-5.4) and from the methanol-MTBE azeotrope to the methanol-(n-butene) azeotrope in the MTBE system (Figure 5.5).

The practical significance of distillation boundaries pertains to the directional effect that fractionation has on the residue composition. For example, a mixture whose composition lies in the upper distillation region of the ETBE residue curve diagram (e.g. 10% ETBE, 60% ethanol and 30%  $C_4$ ) can only be distilled to increase the ethanol purity while a mixture whose composition lies in the region below the boundary (e.g. 60% ETBE, 5% ethanol and 35%  $C_4$ ) can only be distilled towards the ETBE node. Clearly, an ETBE column should be designed to produce a high purity ETBE product so that (at least) the stripping section of the column must be enclosed within the lower distillation region.

Residue curve diagrams are also useful for identifying potential distillation pinch points. Azeotropes in a system introduce curvature in the residue curves. Excessive curvature can indicate a pinch that increases the fractionation requirement. For example, it is easier to increase ETBE purity in a mixture with little ethanol as the residue curves run more smoothly towards the ETBE vertex. In such a separation, the ethanol concentration will initially increase (since the residue trajectories curve towards the ETBE-ethanol azeotrope).

Similar conclusions can be made about the rectifying section of an ETBE column. Clearly, there is an incentive to minimise ETBE (and ethanol) in the distillate product. This can be achieved more readily if there is little ETBE in the rectifying section as the residue trajectories are curved towards the ETBE-ethanol azeotrope. It is theoretically possible to completely eliminate both ETBE and ethanol from the distillate product since there exists a node that corresponds to pure C<sub>4</sub>. However, distillation towards this node places restrictions on the composition of the bottoms product since ethanol must leave the system in at least one product. It is also clear from the ETBE residue curve diagram that it is not possible to produce a distillate product with ethanol but without ETBE. This is different to the MTBE system, where there exists a node that contains only methanol and C<sub>4</sub>.

## 5.1.2 Reactive Residue Curves

### 5.1.2.1 Governing Equations

The residue trajectories change shape if the additional constraint of chemical equilibrium is imposed on the system. In this case, the trajectories are denoted reactive residue curves. The equations that define these curves are similar to those for simple residue curves, modified only by the requisite equations for chemical equilibrium (5.9 and 5.10):

$$\frac{dM}{dt} = -V \quad (5.7)$$

$$\frac{d(Mx_i)}{dt} = -Vy_i \quad (5.8)$$

$$K_{eq} = \frac{a_{ETBE}}{a_{EtOH} \cdot a_{iBut}} \quad (5.9)$$

$$\ln K_{eq} = 10.387 + \frac{4060.59}{T} - 2.89055 \ln T - 0.0191544T + 5.28586 \times 10^{-5} T^2 - 5.32977 \times 10^{-8} T^3 \quad (5.10)$$

$$\frac{d(MH)}{dt} = Q - VH^v \quad (5.11)$$

$$\frac{dH}{dt} = 0 \quad (5.12)$$

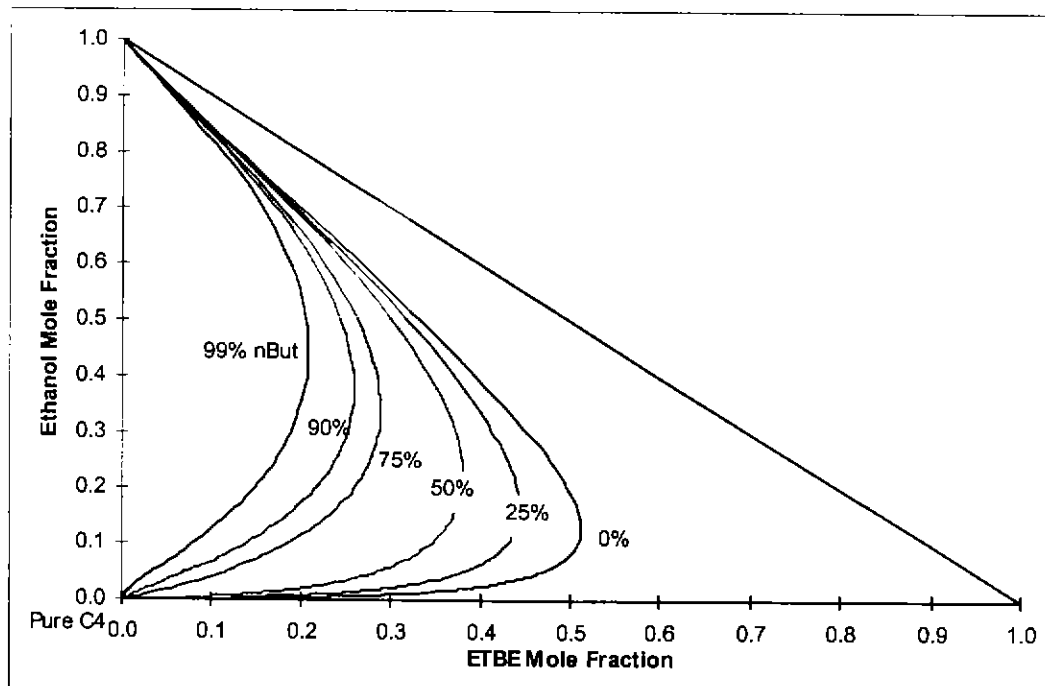
$$P \cdot y_i = \gamma_i \cdot x_i \cdot P_i^{vap} \quad (5.13)$$

$$\sum y_i = 1 \quad (5.14)$$

This system of equations (5.7-5.14) has one less degree of freedom than the corresponding set of equations for non-reactive residue curves (5.1-5.6) since the chemical equilibrium definition requires two new equations but only one new variable ( $K_{eq}$ ). The physical interpretation of this result is that the feed composition cannot be defined independently where chemical equilibrium is assumed. Although any combination of components can be introduced to a reactive still, the composition will change immediately if the mixture is not already in chemical equilibrium.

#### 5.1.2.2 ETBE System

In a ternary system (i.e. ethanol, isobutene and ETBE only), there is only one possible reactive residue curve at any given pressure. In a quaternary system (e.g. with n-butene added to the reactive mixture), the initial amount of n-butene uniquely defines the residue trajectory. Note that this is slightly different to the initial concentration, as the reaction can change the concentration by altering the total number of moles in the system.



**Figure 5.6 - Reactive Residue Curve Diagram for the ETBE System at 950 kPag**

Figure 5.6 shows the residue trajectories for a family of reactive, quaternary mixtures with differing amounts of inert. The n-butene concentrations shown on the diagram indicate the approximate feed composition only. A positive slope (e.g. near the  $C_4$  node) indicates ETBE formation while a negative slope (e.g. near the ethanol node) indicates ETBE decomposition. Although the highest concentration of ETBE is achieved with no inert present, the ETBE synthesis reaction continues with much higher ethanol concentrations when the system is diluted with n-butene.

### 5.1.2.3 MTBE System

Figure 5.7 indicates the reactive residue trajectories for the MTBE system at the same pressure. Interestingly, the effect of the  $C_4$  inerts is greatly diminished. The maximum MTBE concentration is higher than the maximum ETBE concentration (due to the more favourable reaction thermodynamics) but the synthesis reaction cannot be sustained at a methanol concentration above 25%, regardless of the initial inert concentration. The diagram also suggests that the cooling effect of additional  $C_4$  inerts is negligible for initial n-butene concentrations above 50%. Although all of the residue curves originate from the methanol- $C_4$  azeotrope, the trajectories are severely curved near the pure  $C_4$  node that will act as a distillation pinch point.

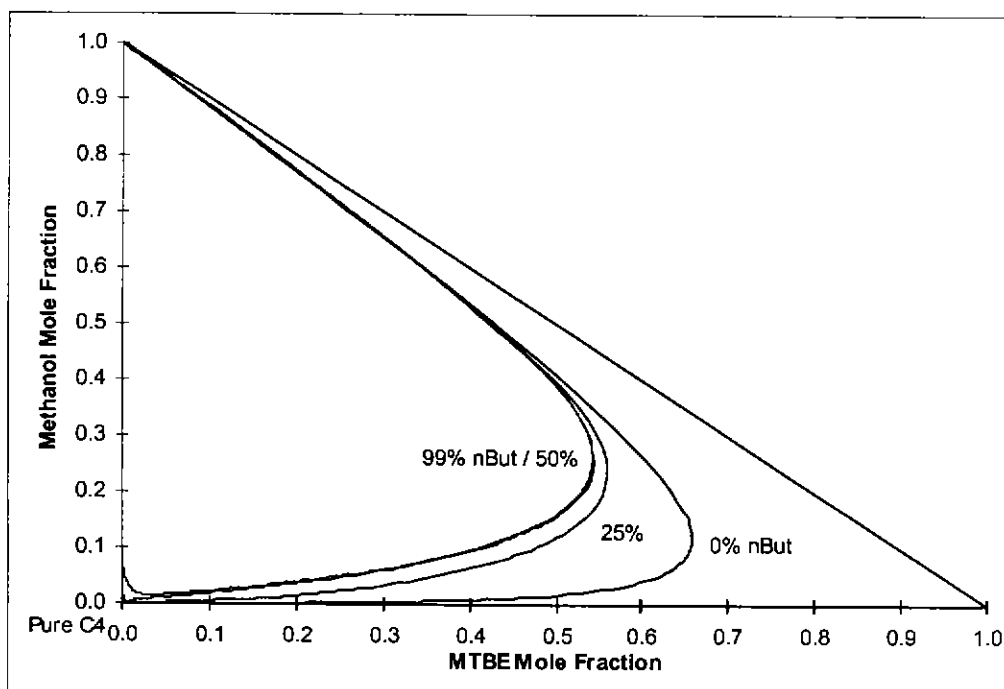


Figure 5.7 - Reactive Residue Curve Diagram for the MTBE System at 950 kPag

#### 5.1.2.4 Kinetically Controlled Reactions

An alternative representation of the reactive still uses a kinetic model of the reaction and requires the specification of a catalyst loading. Under these conditions, the heating rate is important in controlling the residue trajectory. A very slow heating rate combined with any quantity of catalyst will approximate chemical equilibrium while a faster heating rate will suppress the reaction. This effect is demonstrated by Figure 5.8, which compares three trajectories with very low catalyst loadings. The residue trajectories with moderate to high catalyst loadings align closely with the equilibrium curves, thereby confirming that the equilibrium model is appropriate for the ETBE system.

The upper curve in Figure 5.8 corresponds to the lowest catalyst loading. The trajectory is strongly influenced by the shape of the non-reactive residue curve (Figure 5.3), particularly near the  $C_4$  node where the reaction is slowest (due to the colder temperatures implied by the phase equilibrium requirement). As the reaction rate increases with the rising temperature and changing composition, the system approaches reaction equilibrium and the residue trajectory assumes a similar shape to the equilibrium reactive residue curves (Figure 5.6). A higher catalyst loading (e.g. the lower curve in Figure 5.8) results in a trajectory that approximates the reaction equilibrium model more closely.

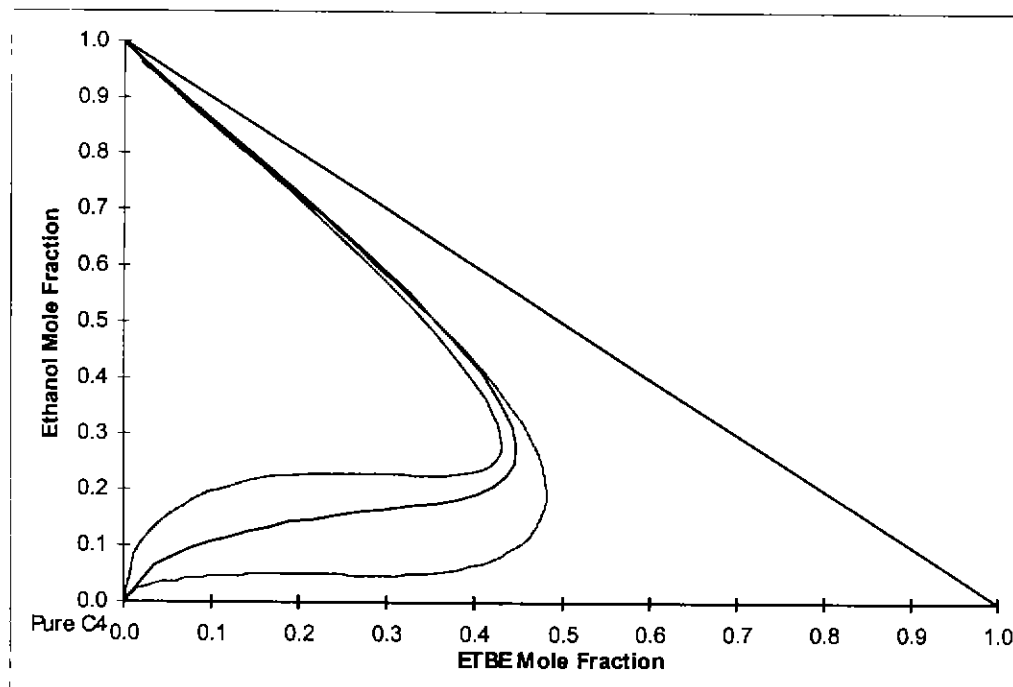


Figure 5.8 - ETBE Reactive Residue Curves (Limited by Reaction Kinetics)

### 5.1.2.5 Significance for Reactive Distillation Column Design

The reactive residue diagrams for both the ETBE and the MTBE system include no azeotropes, only one stable node (ethanol or methanol) and only one unstable node (pure  $C_4$  in the ETBE system or the  $C_4$ -methanol azeotrope in the MTBE system). A pure ether product is not possible in either system. This defines the requirements for hybrid columns for both syntheses. While a stripping section is clearly required to obtain the pure ether product, there is no specific requirement for a rectifying section in either process since both the reactive and non-reactive residue curves converge to the same node. However, a non-reactive section can be seen to purify the distillate product more efficiently and is, therefore, recommended.

The reactive residue trajectories in both the ETBE and MTBE systems all reach a maximum value of the ether concentration before converging towards the ethanol or methanol node. At ethanol/methanol concentrations below the 'turning point' the reaction proceeds to the right (ether synthesis) while the reaction proceeds to the left (ether decomposition) at higher alcohol concentrations. In order to avoid the decomposition reaction, a hybrid column should be designed to produce a reactive section composition profile on the ether synthesis branch of the residue curve. Therefore, the reactive residue curve diagram can be used to provide *a priori* knowledge of the approximate feed compositions to the non-reactive sections, and to determine the approximate influence of the column feed composition on the operating conditions.

The initial concentration of inert  $C_4$  components clearly has a significant effect on the reactive residue trajectory in an ETBE system (Figure 5.6). Although a directionally similar effect is evident from the MTBE reactive residue curve diagram (Figure 5.7), there is a much lesser dependency on the inerts. This observation highlights a key difference between the two systems. A high concentration of inerts in the feed to an ETBE column will significantly increase the ethanol concentration in the stripping section and also increase the likelihood of crossing the non-reactive distillation boundary so that the stripping section would act to purify ethanol rather than ETBE. However, the residue curve diagram does not provide sufficient information to determine whether the additional inerts would have a favourable effect on the synthesis reaction. An MTBE column could be expected to operate similarly over a wide range of feed compositions.

Although both the ETBE and MTBE reactions are essentially limited by thermodynamics rather than kinetics, it is relevant to consider the effect that reaction kinetics have on reactive residue curves for cases when the installed catalyst is poisoned or loses substantial activity.



Figure 5.8 considers such a case and shows that higher ethanol concentrations should be expected in the reaction zone. This suggests that the reactive section is somewhat self-regulating, as the increased ethanol availability will increase the reaction zone temperature and, therefore, increase the reaction rate constant. Although lower isobutylene conversions might be expected as the reaction becomes thermodynamically less favourable, adequate reaction rates should be maintained.

### 5.1.3 Hybrid Residue Curves

A composition transformation has been widely recommended to enhance the applicability of reactive residue curves for reactive distillation design (e.g. Ung and Doherty, 1995; Perez-Cisneros et al., 1996). The transformed co-ordinates allow reactive tie-lines to be drawn and interpreted in a manner which parallels conventional distillation design methods. Essentially, the technique relies on producing a set of co-ordinates that are independent of the reaction. Once this is done, standard geometrical methods can be used to predict the distillate product composition from the feed composition and the bottoms product composition (or vice-versa). This is useful for reactive columns which: (a) do not contain any non-reactive sections; (b) approximate perfect fractionation (i.e. the  $\infty/\infty$  case); and (c) can be satisfactorily represented as a ternary or pseudo-ternary system. Thus, there are significant limitations to applying reactive residue curve analysis to the design of multi-component hybrid systems such as ETBE or MTBE synthesis.

Valuable information can be obtained from both reactive and non-reactive residue curve diagrams but neither describes the complete process. A hybrid residue curve can be constructed by overlaying reactive and non-reactive residue curves (in either transformed co-ordinates or with all  $C_4$  components lumped together). This provides some additional insight but is still not suitable for the design of finite columns.

Figure 5.9 shows ETBE synthesis in a hybrid system at 950 kPag for two cases: no inerts components in the feed; and 95% n-butenes in the feed. No conclusions regarding operating conditions or product compositions can be drawn from this diagram but it shows that both reaction-separation processes are feasible. However, the diagram does provide *a priori* information regarding the composition profiles, from which operating temperatures can be estimated. Figure 5.9 also highlights a sharp change in composition profiles at the intersection of the reactive and stripping sections for the case with no n-butene in the feed. This is potentially a concern as it might indicate a high sensitivity to some (as yet unknown) design parameter.

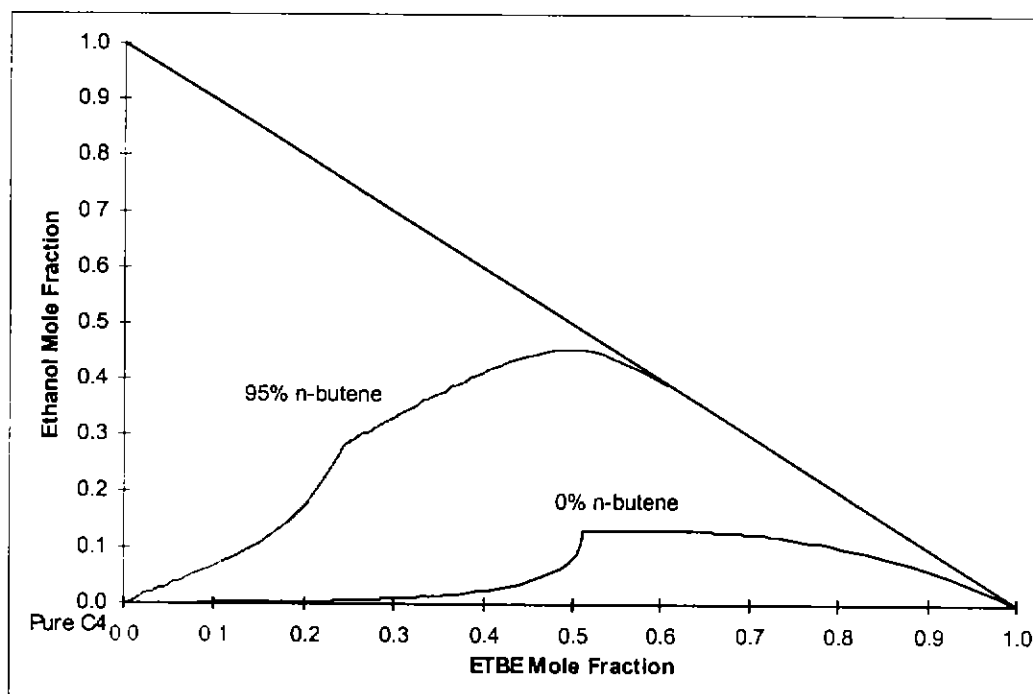


Figure 5.9 - Hybrid Residue Curves for ETBE Synthesis

## 5.2 PROPOSED DESIGN STRATEGY FOR HYBRID REACTIVE DISTILLATION

There is an absence of satisfactory rigorous or empirical design methods for hybrid reactive distillation in the current literature. A practical and effective approach to reactive distillation design has not yet been established. Design tools such as residue curves and reactive residue curves are applicable for preliminary design proposals and screening studies (i.e. determining the feasibility of a given reaction-separation) but are not suitable for detailed design. In particular, these methods do not reflect the influence of the column vapour-liquid loading which is a primary consideration in column design.

A conventional distillation design strategy relies on determining the minimum reflux ratio and the minimum number of ideal stages required for a specified separation. This approach cannot be used for reactive distillation as the separation cannot be specified independently of the reactant conversion. Similarly, conventional short-cut methods are not applicable to reactive distillation. Once the traditional design methods have been necessarily abandoned, rigorous column simulations must be employed. Fortunately, computational power and available modelling techniques are now sufficient to prevent this from being an overly onerous task.

Many simulation cases can be run within several hours but a directionless search still lengthens the design process and risks a non-optimal solution. A focussed design strategy is proposed in Table 5.1. It is important to note that the design process should be iterative and a successful design may require several revisions of the operating conditions. Figure 5.10 provides a diagrammatic representation of the proposed design process and indicates where the process may become iterative by showing recycle steps in dashed lines. Each box represents a task or a design decision that must be resolved before progressing further. The basic rationale for the various recycle loops is as follows:

- The effect of the operating pressure on the reaction rate and the product compositions is strongly dependent on external factors. The optimum will vary substantially between installations and rigorous simulations provide the only effective method of optimisation (see Section 4.1.4).
- The reflux ratio should be increased if the resulting hydraulic loading is insufficient to support a column diameter of at least 1.2 m (suggested practical minimum).
- The column diameter effectively determines the internal layout and imposes restrictions on the distributor design and packing arrangement. Standard configurations might be unsuitable for some column diameters thereby requiring novel designs or a revision of the reflux ratio.
- The principal variables that most affect the process design are the reactant excess, the overhead pressure and the reboiler duty. It is, therefore, important to establish the effects of each of these before finalising a process design.

Table 5.1 - Proposed Design Strategy for the Hybrid Reactive Distillation of Fuel Ethers

Stage	Items	Considerations
1. Design Basis	a) hydrocarbon feed composition	A isobutene rich feed improves energy efficiency but increases reaction zone temperatures. A isobutene lean feed increases the minimum column diameter but has a cooling effect on the reaction zone.
	b) target ether purity	The purity target is dependent on blending requirements but there are usually no specific constraints on conversion.
	c) target hydrocarbon conversion	
2. Reaction	d) stoichiometric excess	Excess alcohol is required to prevent side-reactions. High excess favours conversion; low excess favours purity.
	e) column pressure	Increasing pressure raises temperatures in the column increasing the reaction rate but reducing the equilibrium constant. Relative volatility decreases with pressure. Pressure has an indeterminate effect on the internal composition profile.
3. Distillation	f) key components	The key components in both non-reactive column sections determine the effect of increasing fractionation.
	g) 'minimum' reflux ratio	The minimum reflux ratio cannot be determined using conventional techniques but performance declines rapidly if the reflux ratio is too low. Reflux promotes separation and reaction by recycling the light reactant to the reaction zone.
	h) minimum hydraulic loading	A minimum column diameter of 1.2 m is suggested for catalyst installation and removal.

**Table 5.1 (cont.) - Proposed Design Strategy for the Hybrid Reactive Distillation of Fuel Ethers**

Stage	Items	Considerations
4. Column Topography	i) reactive stages	Should be sufficient to allow enough catalyst to be installed to provide a relatively long cycle time between replacements.
	j) rectifying stages	Optimise to eliminate ether from the distillate but allow light reactant to return to the reaction zone.
	k) stripping stages	Optimise to provide required ether purity without starving the reaction zone of the heavy reactant.
	l) stage efficiencies	High rectifying efficiencies and moderate stripping efficiencies can be expected. Testing required for novel reaction zone packings.
5. Heat Transfer	m) reboiler	Optimised for maximum purity or conversion.
	n) condenser	Determine duty from rigorous simulation.
6. Column Dimensions	o) height	0.6-1.2 m per actual stage. Redistributor required at top of reactive section.
	p) diameter	70-80% flood in non-reactive sections. Testing required for novel reactive packings.
7. Optimisation	q) pressure, reflux and reboiler duty	Some synergies may be realised between key design variables.

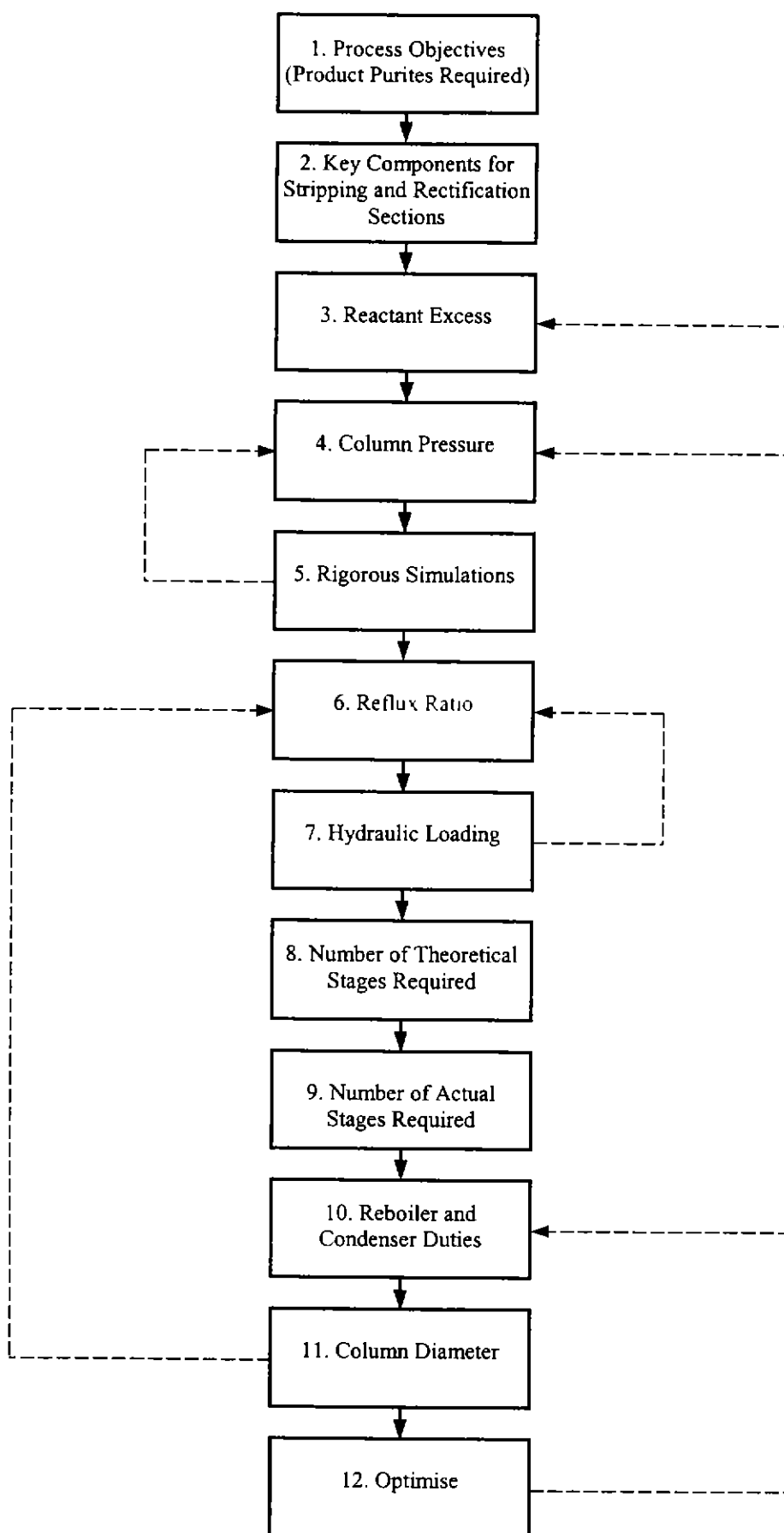


Figure 5.10 - Flow Chart for Reactive Distillation Design

## **CHAPTER SIX**

### **DESIGN ISSUES III - INTEGRATED PLANTS FOR ETBE**

- 6.1 ETBE Synthesis Routes**
  - 6.1.1 Production Alternatives
  - 6.1.2 ETBE Production in a Conventional MTBE Unit
    - 6.1.2.1 Pretreatment
    - 6.1.2.2 Reaction
    - 6.1.2.3 Purification
    - 6.1.2.4 Recovery System
  - 6.1.3 ETBE Production in a MTBE Unit Reactive Distillation
  - 6.1.4 Conventional ETBE Process Without Ethanol Recycle
  - 6.1.5 Reactive Distillation ETBE Process Without Ethanol Recycle
- 6.2 Process Selection**
  - 6.2.1 Applicability of Reactive Distillation to ETBE Synthesis
  - 6.2.2 Operating Constraints Within a Refinery Environment
  - 6.2.3 Optimal Process for an Isobutene-Rich Feed
    - 6.2.3.1 Conventional Process
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    - 6.2.3.4 ETBE-Specific Reactive Distillation Designs
  - 6.2.4 Optimal Process for an Isobutene-Lean Feed
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  - 6.2.5 Process Comparison for ETBE Production
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  - 6.3.1 Requirement for Optimisation
  - 6.3.2 Optimisation Procedure and Techniques
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    - 6.3.3.2 Supervisory Control System
  - 6.3.4 Effectiveness of Process Optimisation
- 6.4 Overall Summary of Findings on Design Issues**

## 6.1 ETBE SYNTHESIS ROUTES

### 6.1.1 Production Alternatives

The history of ETBE is intimately linked with MTBE. It has only ever been promoted as an alternative to MTBE and, because of the inherent similarities between the two agents, it is natural to consider MTBE production methods for ETBE. Indeed, a superficial examination of the problem would suggest that simply processing ethanol (instead of methanol) through the same equipment would be sufficient to produce ETBE, albeit with a yield penalty due to the less favourable reaction equilibrium. However, important differences in the VLE require a more considered approach, especially for reactive distillation, to maximise the potential of ETBE.

There are essentially two main processes for MTBE production, although there are numerous competing technologies with subtle differences. A typical process that employs only conventional technology utilises two catalytic reactors in series followed by a purification column and recovery equipment to recycle unreacted methanol. The reactive distillation process retains most of the items from the conventional process but combines the second reactor with the purification column. In each case, some pretreatment is required to protect the catalyst.

### 6.1.2 ETBE Production in a Conventional MTBE Unit

The four main process steps in the conventional MTBE process are: (a) pretreatment to remove potential catalyst poisons from the feed streams; (b) reaction (usually two stages); (c) purification of the ether product; and (d) recovery of the unreacted alcohol for recycling. This configuration is shown in Figure 6.1 and is directly applicable to ETBE production.

#### 6.1.2.1 Pretreatment

The pretreatment stage is common to all ether synthesis processes where a catalyst is used. The design of the pretreatment equipment and its operation is dependent on the concentration of potential poisons that are expected to be present, and also the catalyst cycle life required. Typical installations include water washing, selective dehydrogenation and/or dual ion exchange resin switch beds that are cycled (one on, one off) due to the fast deactivation of the resin.



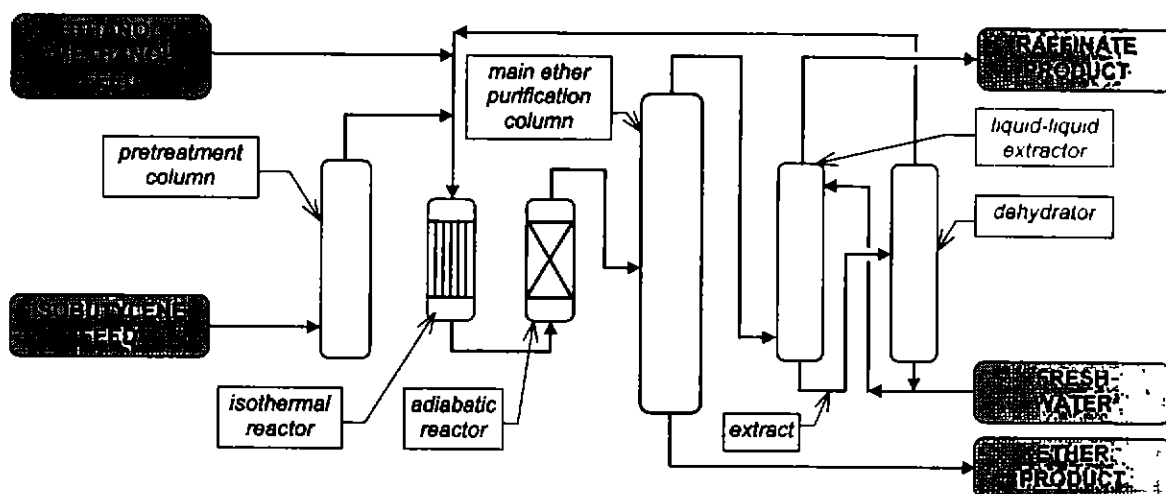


Figure 6.1 - Conventional Ether Synthesis Route

### 6.1.2.2 Reaction

The ETBE reaction is kinetically controlled at low temperatures and thermodynamically controlled at higher temperatures. Operating with only a single reactor would require a very large reactor volume to attain a satisfactory conversion (the reaction rate is always less than 0.2 mol/hr/g catalyst at reaction temperatures below 60°C), or would be restricted to relatively low isobutene conversion (the maximum stoichiometric conversion at 80°C is only 80%). Therefore, there is a considerable incentive to install two reactors in series. The first reactor should operate in the thermodynamically controlled region at high temperature in order to perform the majority of the reaction with a relatively small catalyst volume. The second reactor should operate in the kinetically controlled region to increase the overall conversion.

In an adiabatic reactor, the temperature increases sharply when reaction rates are high due to the exothermic nature of the ETBE reaction. This creates two problems: firstly, the reaction can shift from the kinetically controlled region to the thermodynamically controlled region and reduce the overall, final conversion; and secondly, localised reactor hot spots can develop which deactivate and thermally degrade the catalyst (ion exchange resin is generally unstable at temperatures above 120°C). The preferred solution to these problems is to operate the first reactor isothermally by circulating water between the reactor tubes (Miracca et al., 1994). The second reactor can still be operated adiabatically (thereby reducing the capital cost of the reactor) as much less heat is released and the subsequent temperature rise across the reactor is small (normally 10°C or less).

The design and operation of a dual reactor system should be optimised to minimise the installed reactor volume and, therefore, to maximise the catalyst cycle life. The reaction rate at any point is dependent on the temperature and composition at that point. The concentration of all components must be known, not just those taking part in the reaction. The following equations apply to a two reactor system where the first reactor is operated isothermally at  $T_1$  and the second reactor is operated adiabatically with an inlet temperature of  $T_1$  and an outlet temperature of  $T_2$ :

*Specific Weight of Catalyst Required in a Dual Reactor System*

$$M_c = \int_0^{x_1} \frac{1}{r_A} dx + \int_{x_1}^{x_2} \frac{1}{r_B} dx \quad (6.1)$$

*ETBE Reaction Rate in an Isothermal Reactor*

$$r_A = k_{rate} \cdot \left( \frac{a_{iBut}}{a_{EtOH}} - \frac{a_{ETBE}}{K_{ETBE} a_{EtOH}^2} \right) \quad (6.2)$$

$$k_{rate} = 1.209 \times 10^{12} \exp\left(-\frac{87.2}{RT_1}\right) \quad (6.3)$$

$$\ln K_{ETBE} = 10.387 + \frac{4060.59}{T_1} - 2.89055 \ln T_1 - 0.0191544 T_1 + 5.28586 \times 10^{-5} T_1^2 - 5.32977 \times 10^{-8} T_1^3 \quad (6.4)$$

*ETBE Reaction Rate in an Adiabatic Reactor*

$$r_B = k^*_{rate} \cdot \left( \frac{a_{iBut}}{a_{EtOH}} - \frac{a_{ETBE}}{K^*_{ETBE} a_{EtOH}^2} \right) \quad (6.5)$$

$$k^*_{rate} = 1.209 \times 10^{12} \exp\left(-\frac{87.2}{RT^*}\right) \quad (6.6)$$

$$\ln K_{ETBE} = 10.387 + \frac{4060.59}{T_1} - 2.89055 \ln T_1 - 0.0191544 T_1 + 5.28586 \times 10^{-5} T_1^2 - 5.32977 \times 10^{-8} T_1^3 \quad (6.7)$$

$$\Delta H_r = \dot{m} \int_{T_1}^{T_2} c_p dT^* \quad (6.8a)$$

$$T^* = T_1 + \frac{\Delta H_r}{\dot{m} c_p} \quad (6.8b)$$

The right hand side of equation (6.1) should be minimised for a selected value of  $x_2$  to find  $T_1$  and  $x_1$ , where  $T^*$  is evaluated at each incremental value of  $x$  in the adiabatic reactor. If  $T_2$

is relatively close to  $T_1$ , equation (6.8b) is a good approximation to equation (6.8a) and can be used to calculate  $T^*$  more easily. The relationship between  $a_i$  and  $x_i$  will vary and should be calculated at each incremental value of  $x$  using the UNIFAC equations or a similar activity coefficient model.

The results of the above optimisation will vary with the selected value of  $x_2$  (the final conversion) and the composition of the hydrocarbon feed stream to be used. Other factors, such as the relative cost of the tubular, water-cooled reactor and the adiabatic packed-bed reactor, are not incorporated in the above equations but should be considered in order to reflect local economics. The optimised value of  $T_1$  can be used to size both the isothermal and the adiabatic reactor, via equation (6.1). The results of a semi-rigorous optimisation using equations (6.1) to (6.8) suggest that an isothermal reactor temperature of approximately 80°C is optimal to reach a final isobutene conversion of 90% at the outlet of the second reactor.

Ideally, the process reactants should always be supplied in a stoichiometric ratio to minimise their concentration in the reaction product. However, feeding an excess of ethanol to the reactors has two significant advantages for ETBE synthesis: firstly, it increases the conversion of isobutene by Le Chatelier's principle; and secondly, it minimises the dimerisation side-reaction by effectively maintaining the catalyst surface covered with ethanol (Kitchaiya and Datta, 1996). The ETBE purity decreases rapidly as the ethanol excess increases so that an excess of around 5% is preferred for most conditions.

#### 6.1.2.3 Purification

The reaction product contains small quantities of unreacted ethanol and isobutene and up to 80% inert  $C_4$  hydrocarbons (mostly n-butenes, isobutane, n-butane and/or butadiene, depending on the source of the hydrocarbon). The Reid vapour pressure (RVP) of these components is generally too high to be blended directly into the gasoline pool. Even small quantities (less than 1%) are sufficient to substantially suppress the boiling point and the flash point of the mixture and, therefore, need to be removed from the reaction product before gasoline blending. Distillation is the simplest and most effective means of separation, although the presence of azeotropes restricts the range of feasible distillation product compositions. Most significantly, the azeotrope between ethanol and ETBE prevents an ethanol-free ETBE product from being distilled without losing a considerable quantity of ETBE in the distillate. At higher pressures, azeotropes also form between ethanol and various  $C_4$  components. These azeotropes result in a small concentration of ethanol always being present in the distillate.

The design of the purification column is dependent on the specification of both the ether and distillate products. A low  $C_4$  concentration in the bottoms product (less than 0.1%) is required while the loss of ETBE in the distillation should be minimised. The design of the purification column can be optimised using conventional techniques for distillation design (e.g. see Kister, 1994), although the combination of a very high number of stages and a low reflux ratio could result in an impractical design (i.e. too tall and too thin) due to the relatively low feed rates which are often used for etherification units. Typically, around 30 ideal stages is sufficient to meet the design requirements with a practical reflux ratio. A higher number of stages (or a higher reflux ratio) will reduce the concentrations of  $C_4$  in the ether and ethanol in the distillate, and might be desirable for some refinery configurations. Similarly, if the ether product specification is less stringent, fewer stages and/or a lower reflux ratio might be adequate.

#### 6.2.3.4 Recovery System

MTBE processes have been developed to include a recovery system that removes and recycles methanol from the distillate. This is required because of the azeotrope between methanol and isobutene (and also other  $C_4$ s) which contains around 10% methanol. As a consequence of the azeotrope, if the stoichiometric excess of methanol is below a critical value (around 40% for isobutene-rich feeds), methanol is preferentially recovered in the distillate product rather than the bottoms product. Some means of recovering this methanol must, therefore, be installed to avoid the loss of valuable raw material and remove the risk of downstream contamination or catalyst deactivation. The simplest method for achieving this is a water wash (which is highly selective in separating the hydrophilic methanol from the hydrophobic hydrocarbons) followed by a methanol-water distillation.

The same considerations do not always apply to ETBE units. Most significantly, the ethanol concentration in the distillate product is usually substantially lower (less than 1%). Therefore, the incentive to provide any form of recovery is significantly reduced. Secondly, the azeotrope between ethanol and water results in at least some water always being recycled to the reaction stage with the recovered ethanol. The water introduced to the system immediately reacts to form isobutanol and, thereby, decreases the yield of ETBE and the purity of the ether product. Since the ratio of fresh ethanol to recovered ethanol is around 100, the ingress of water is relatively minor and the same equipment (water wash plus ethanol-water distillation) can be used with only a slight effect on the ether purity (usually only around 1%). In practice, the need for ethanol recovery equipment will be

determined primarily by downstream processing requirements and restrictions but the justification for additional equipment is much weaker than for MTBE production.

### 6.1.3 ETBE Production in a MTBE Reactive Distillation Unit

The reactive distillation process for MTBE differs from the conventional process in the combination of the second reaction stage (adiabatic) with the purification column and the elimination of some peripheral equipment. The modified process is depicted in Figure 6.2.

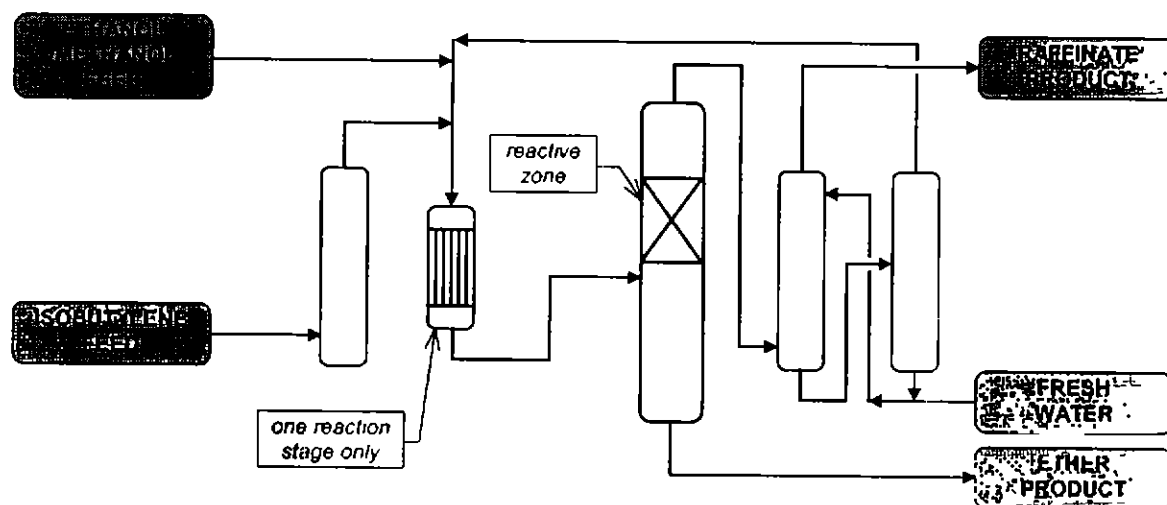


Figure 6 2 - Ether Synthesis Via Reactive Distillation

The pretreatment stage is unaffected. The operation of the first reaction stage (isothermal) can also remain unchanged. Although it is technically possible to perform all of the reaction inside a reactive distillation environment, it is not practical to do so due to the difficulty of installing and removing catalyst from inside the column. Retaining the first reaction stage from the conventional process unloads the catalyst inside the column and provides further protection against deactivation. It also reduces the amount of heat liberated inside the column which might otherwise produce problems (e.g. localised flash boiling). Slightly higher conversions can also be achieved by retaining the primary reaction stage.

The purification column used in the reactive distillation process differs from that used in the conventional process with the installation of catalyst on trays or packed sections above the feed point. Some non-reactive stages are still required above and below the reactive section to produce the necessary separation between products and reactants. The reactive distillation column is, therefore, actually a hybrid column that contains a reactive distillation section and two non-reactive distillation sections.

The column operating conditions required in the reactive distillation process are comparable to what would be used in the conventional process. Similar overhead pressures should be used in both reactive and non-reactive distillation columns. A similar reboiler duty should be used too. This produces an increase in the condenser duty as the heat of reaction effectively adds to the column heat input. However, the additional vapour-liquid traffic created by the higher condenser duty (and higher overall heat input) maximises the benefits of adding the catalyst. The only really worthwhile change suggested for the reactive distillation process is to move the feed-point a few stages closer to the condenser. This improves the overall performance of the column by making it easier to achieve high ether product concentrations. Further optimisation can be undertaken but the advantages of reactive distillation should already be evident after these simple changes. The operation of the recovery system should also remain essentially unchanged as the only differences arise through slight compositional changes in the distillate product.

### **6.1.3 Conventional ETBE Process Without Ethanol Recycle**

The absence of any significant azeotrope between ethanol and butenes results in unreacted ethanol being recovered primarily with the ETBE product. As indicated above, the presence of an azeotrope between ethanol and water also results in some water being recycled to the reaction stage if it is attempted to recover the unreacted ethanol from the distillate. There is much lower load on the recovery equipment due to the lower concentration of ethanol in the distillate. In fact, it is feasible, under some refinery conditions, to eliminate the ethanol recovery equipment altogether, resulting in the simplified flow diagram shown in Figure 6.3.

### **6.1.5 Reactive Distillation ETBE Process Without Ethanol Recycle**

A reactive distillation process for ETBE synthesis would utilise the same principles as the MTBE process and should yield the same benefits of increased conversion, increased energy efficiency and reduced capital cost. The majority of the reaction (say, 80%) would be performed in an isothermal, tubular reactor operating at moderate conditions of temperature (around 90°C) and pressure (1500-2000 kPa to ensure all components remain in the liquid phase). The feed to the reactive distillation column would, therefore, be rich in ETBE but still contain some ethanol and isobutene. The products from the bottoms and overheads of the reactive distillation column would be ETBE with some ethanol, and non-reactive hydrocarbon with a small amount of isobutene and ethanol, respectively. The distillate product may or may not require further processing depending on its composition and the refinery configuration. This scheme is shown in Figure 6.4 without ethanol recovery equipment.

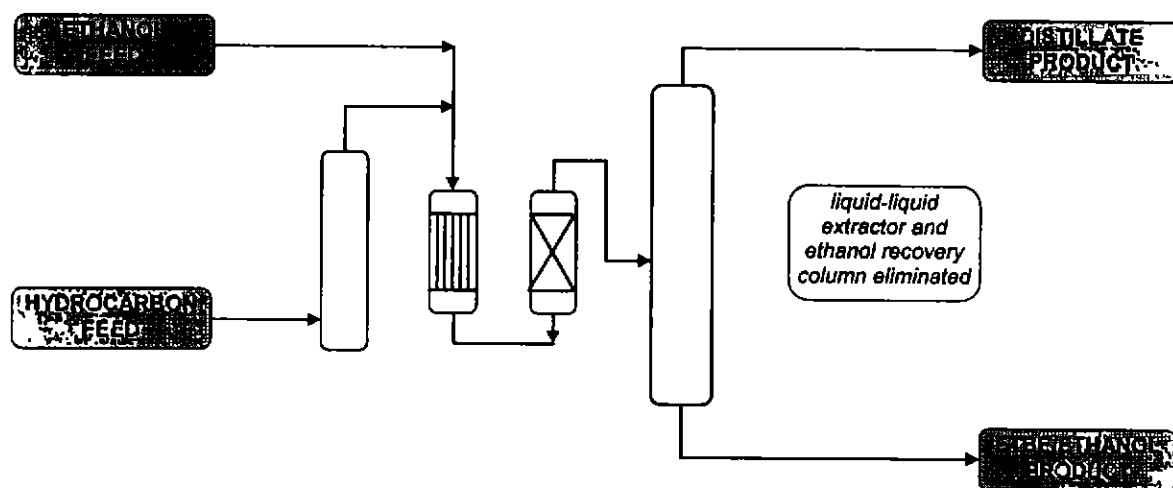


Figure 6.3 - Conventional ETBE Synthesis Route Without Ethanol Recycle

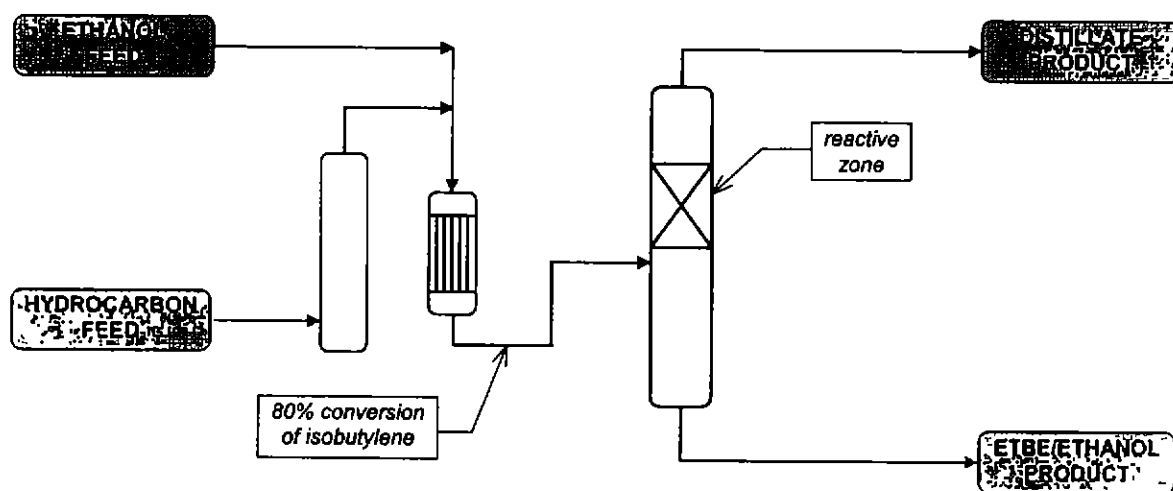


Figure 6.4 - Reactive Distillation Process for ETBE Without Ethanol Recycle

## 6.2 PROCESS SELECTION

### 6.2.1 Applicability of Reactive Distillation

The reactive distillation process for MTBE quickly gained acceptance in the market place after the first commercial application was installed in 1981 (Smith and Huddleston, 1982). Today, most of the new MTBE plants which are currently in either the planning or construction phases will use processes based around reactive distillation (Riddle, 1996). Although the advantages which reactive distillation brings to MTBE production are well recognised, it is not clear whether the same benefits can be realised for ETBE synthesis.

The most obvious difference between the MTBE and ETBE reaction systems is the more restrictive ETBE thermodynamics. This implies a lower isobutene conversion at the same temperature but it does not preclude the use of reactive distillation. Indeed, the improvement in the stoichiometric ratio of reactants is potentially even more advantageous since there is more to gain. The ETBE reaction rate is similar to MTBE so that the required catalyst volume should not be prohibitive. The reaction is also equally selective (up to 99%) so that the side-reactions (predominantly dimerisation and hydration) are not likely to be any more significant.

Ethanol and ETBE are less volatile than methanol and MTBE, leading to higher distillation temperatures at the same pressure. This would result in a faster reaction rate but a lower equilibrium constant, although the operating pressure could be adjusted to mostly compensate for the VLE differences. The most important distinction in the phase behaviour of the two systems is the absence of azeotropes between ethanol and butenes at pressures below approximately 1400 kPag. Comparable azeotropes in the MTBE system are important in recycling methanol to the reaction zone and this variance suggests that a slightly different operating strategy might be required, notably that excess ethanol should be recovered with the bottoms rather than the distillate. The absence of these azeotropes will also affect the reaction via changes in the internal distribution of components although the exact effect is hard to predict without detailed simulations.

Overall, there appear to be sufficient similarities between the MTBE and ETBE systems to suggest that reactive distillation could deliver productivity gains to ETBE manufacture that are similar to those already demonstrated for MTBE. However, there are also enough differences between the two systems to indicate that specialised designs might be required to maximise the process benefits that could be obtained from reactive distillation.



### 6.2.2 Operating Constraints Within a Refinery Environment

It is important to consider the integration of an ETBE unit within an operating refinery complex. In particular, only feeds that are readily available can be used and consideration must be given to the life-cycle of a unit (i.e. the time required between periodic maintenance or catalyst replacement).

High purity isobutene is generally not available within a refinery complex, nor is it necessarily desirable as it makes control of the reactor temperature difficult (more heat is released per unit of feed for high purity feeds). However, isobutene is present in significant concentrations in the products of several refining processes, particularly steam cracking and catalytic cracking. The other components present in the products of these units are usually other  $C_4$  hydrocarbons and mostly olefinic. A typical steam cracker product will contain 40% isobutene, 30% n-butenes and 30% butadiene while a typical catalytic cracker  $C_4$  product will contain 15% isobutene, 35% n-butenes, 40% isobutane and 10% n-butane (Miracca, 1996; Jensen, 1996). These compositions will vary somewhat with the crude source, and also the type and activity of the catalyst used in catalytic cracking. Isobutane dehydrogenation can also be the source of isobutene and very high purities (95%+) are sometimes achievable, in which case dilution with another  $C_4$  stream is desirable for etherification.

Ethanol, whether sourced from renewable material (biomass) or from ethylene, is usually manufactured to a high purity to essentially eliminate water. Azeotropic ethanol is widely available but is not recommended for etherification processes as the water reacts quickly with isobutene to form isobutanol. While isobutanol can itself be used as an octane enhancer and oxygenate, its properties make it less suitable than ETBE for gasoline blending. The commercial value of isobutanol is also lower than ETBE, so that the hydration reaction should always be minimised.

The fluids involved in the ETBE process are mostly non-fouling and non-corrosive so that the life-cycle of a unit would most likely be determined by the degradation of catalyst activity in either a fixed-bed reactor or the reactive distillation column. The catalyst is poisoned by salts, basic compounds such as nitriles, and sulphur compounds that may be found in potential hydrocarbon feed streams. Consequently, a guard chamber (or similar pretreatment equipment) is essential to remove contaminants before they reach the reactor(s). This equipment would take on added importance in a reactive distillation unit as the task of replacing the catalyst inside a column is significantly more difficult.

### 6.2.3 Optimal Process for an Isobutene-Rich Feed

As noted previously, isobutene can be sourced from several process units within a large refinery complex. The two most common sources of isobutene for etherification are steam cracking units (35-50 wt% isobutene) and catalytic cracking units (10-25 wt% isobutene). This section examines the implications of processing  $C_4$  hydrocarbon from a steam cracking unit (SCU) and the effect it has on process selection.

A typical SCU product composition of 40% isobutene, 30% n-butenes and 30% butadiene, was assumed as the ETBE unit feed. Process designs were completed for a 5000 kg/hr (1000 bbl/day) ether unit using (a) conventional technology, (b) a reactive distillation column that was designed for MTBE synthesis, and (c) two designs which were specifically tailored for ETBE synthesis. For each type of system, an optimised MTBE design (with 5% excess methanol in the feed) was used as the base case and then two ETBE designs were completed, with and without a 5% stoichiometric excess of ethanol. The cases with an excess of ethanol should produce the highest isobutene conversions while the cases with only stoichiometric ethanol should produce the highest purity ETBE products. It is important to recognise that, where a stoichiometric excess of ethanol is not used, the rate of formation of DIB will be higher (Kitchaiya and Datta, 1996).

#### 6.2.3.1 Conventional Process

This design comprises a two-stage reactor with an intercooler and a purification column, and conforms closely to the process flow diagram shown in Figure 6.1. The first reactor operates isothermally at 80°C. The intercooler cools the reactor effluent to 40°C before the second reaction stage that is operated adiabatically. This represents a reaction scheme that is close to the optimum for ETBE synthesis where the target isobutene conversion is 90%.

The effluent from the second reactor is purified by a distillation column with 30 ideal stages (the condenser is stage 1 and the reboiler is stage 30), operating with an overhead pressure of 700 kPa. This is considered to be typical of industrial MTBE processes, although a wide variation inevitably exists due to variances in product specifications and feed compositions. The feed point, stage 18, was optimised using rigorous simulations of the column. An ether product composition with 0.01%  $C_4$  was specified, based on the potential detrimental influence on the product volatility of a higher  $C_4$  content. This was achieved with a reflux ratio of 1.2. The pretreatment stage and ethanol recovery equipment were not simulated as they are essentially independent of the process design optimisation.

Pro/II (SimSci, 1994) was used for all the simulations undertaken here. Chemical equilibrium was assumed at both reactor outlets corresponding to a case with surplus catalyst (e.g. plant start-up). The ETBE reaction model of Jensen and Datta (1995) was used to provide the necessary equilibrium data. The UNIFAC model was used to predict the liquid phase non-idealities and all calculations were made in terms of component activities rather than concentrations. Other physical properties were predicted with the Soave-Redlich-Kwong equation of state. This combination of reaction data and physical property methods was used successfully in Chapter 3 and was validated against experimental data for an MTBE column.

The reactor feed rate (hydrocarbon plus ethanol) was scaled to produce exactly 5000 kg/hr of ether for the MTBE case and each of the ETBE cases (with and without an ethanol excess). The key simulation results for both cases are shown in Table 6.1. The net oxygen production rate (kg/hr of oxygen in the ether product) and consumption of raw materials per kg of ether were calculated for each case to facilitate an effective comparison between cases. These results, plus the isobutene conversion and ETBE purity have been highlighted.

The oxygen production rate includes a contribution from both the ether product and the alcohol reactant but the methanol contribution in MTBE production is normally negligible due to the high MTBE purity. For ETBE, 11-14% of the net oxygen production comes from ethanol contained in the ether product. This essentially balances the higher oxygen content of MTBE compared with ETBE so that there is no clear advantage for either ether. The net isobutene consumption is roughly equivalent in each system but MTBE production is much more economical with respect to the consumption of the alcohol reactant. The difference arises from (a) the more favourable stoichiometry of the MTBE reaction, (b) recycling methanol from the distillate in the MTBE process and (c) the relatively small concentration of methanol in the MTBE product. The ETBE reaction produces a higher mass yield of product but this is balanced by the lower conversion.

Table 6.1 - Conventional Processes for ETBE and MTBE (Isobutene-Rich Feed)

	<b>MTBE with 5% Excess Methanol</b>	<b>ETBE with 5% Excess Ethanol</b>	<b>ETBE with Stoichiometric Ethanol</b>
Reactor Feed Rate (kg/hr)	10,400	10,260	10,330
Second Stage Reactor Outlet Temperature (°C)	48	54	54
iBut Conversion: 1st Reaction Stage	88.0%	79.6%	78.0%
2nd Reaction Stage	61.4%	53.8%	48.9%
Overall	<b>94.8%</b>	<b>90.0%</b>	<b>88.3%</b>
Bottoms Composition (wt%)	<b>99.2% MTBE,</b> 0.01% MeOH, 0.8% DIB	<b>92.5% ETBE,</b> 6.8% EtOH, 0.7% DIB	<b>93.9% ETBE,</b> 5.4% EtOH, 0.7% DIB
Distillate Composition (wt%)	2.6% iBut, 93.4% other C <sub>4</sub> s, 3.7% MeOH	5.6% iBut, 94.3% other C <sub>4</sub> s, 0.15% EtOH	6.6% iBut, 93.2% other C <sub>4</sub> s, 0.14% EtOH
Oxygen Production Rate (kg/hr)	<b>915</b>	<b>913</b>	<b>885</b>
Net Alcohol Consumption (kg/kg ether)	<b>0.365</b>	<b>0.526</b>	<b>0.511</b>
Net Isobutene Consumption (kg/kg ether)	<b>0.832</b>	<b>0.821</b>	<b>0.826</b>
Reboiler Duty (MW)	1.58	1.40	1.43
Column Diameter (mm)	1200	900	900

Overall, the two most important disadvantages of the ETBE process are the low isobutene conversion and the low ETBE product purity. The isobutene conversion in the reactor is around 5% lower than would be achieved in MTBE production. This increases the consumption of both raw materials. The ETBE product purity is 5-7% lower than would be achieved in MTBE production. This further increases the ethanol consumption as ethanol contained in the column bottoms product remains with the ETBE product, even if downstream recovery/recycling equipment is present.

The ETBE process does, however, have two advantages. Firstly, the reboiler duty is 10-12% lower than required for MTBE production. This is primarily because ethanol is recovered preferentially in the bottoms product rather than the distillate. The resulting boilup rate and vapour flow up the column is, therefore, lower than the MTBE process and the column diameter can be reduced accordingly. Secondly, the distillate from ETBE synthesis contains only 0.14-0.15% ethanol.

A low concentration of ethanol in the distillate is potentially advantageous as it might allow the ethanol recovery equipment (shown downstream of the purification column in Figure 6.1) to be retired with some saving in operating expenses. The main considerations here are the possible poisoning of catalysts in downstream process units and the potential saving in raw material costs. As the ethanol concentration in the distillate decreases, both of these factors become less important. The use of recovery equipment incorporating a water wash also creates a risk of water contamination of the reactor feed following process upsets. Even during normal operation, the ethanol-water azeotrope will introduce small quantities of water into the system leading to isobutanol formation. Although the recovery equipment might feasibly be eliminated from the ETBE process, it should be considered essential for MTBE production as the distillate product contains over 3% methanol and recovery can be effected without contaminating the recycle stream with water (due to the absence of an azeotrope in the methanol-water system).

Comparing the two ETBE cases, a stoichiometric excess of ethanol increases the ethanol consumption but reduces the isobutene consumption. The optimal stoichiometric excess should be optimised with respect to the price and availability of each raw material while also considering the effect of excess ethanol on the reaction selectivity (the DIB reaction is suppressed even at low values of excess) and the acceptable level of ethanol in the ether product.

ETBE has a slightly higher value than MTBE due to its lower RVP and better blending characteristics. However, overall, ETBE production is unlikely to be competitive with MTBE unless ethanol can be obtained very cheaply.

#### *6.2.3.2 Reactive Distillation Process*

Reactive distillation columns for MTBE synthesis are now commonplace. Several sources suggest that these columns can also be used for ETBE synthesis (e.g. Petrochemical Processes, 1995). To test this hypothesis, a reactive distillation system was designed and optimised for MTBE production, and then simulated using Pro/II which now contains a reactive distillation module (version 4.01 onwards). Suggested operating conditions for producing MTBE from an isobutene-rich feed using reactive distillation, and the predicted process results are shown in Table 6.2. It can be clearly seen (by comparison with Table 6.1) that this technology performs better than the conventional process, especially with respect to the isobutene conversion obtained.

The reactive distillation column used in the simulations was simply modified from the column used for the non-reactive distillation cases presented above, i.e. 30 ideal stages. This reflects the capacity for revamping conventional processes for reactive distillation with only limited capital input. Many of the existing reactive distillation etherification units are merely conventional processes which have been revamped to eliminate the second reactor and incorporate catalyst into the ether purification column. The simulations of the reactive distillation system were completed by fixing the column reboiler duty at the values used for the non-reactive distillation case, while allowing the reflux ratio to increase slightly due to the heat liberated by the reaction which contributes to the heat input to the column. The only change from the configuration used previously was that the feed point was shifted to stage 15 (from stage 18). This was done to increase the number of stages available for ether stripping below the feed-point to allow high ether product concentrations to be retained.

The same equipment was then simulated for ETBE synthesis, for cases with and without a stoichiometric excess of ethanol. Again the reboiler duty was maintained constant from the non-reactive distillation cases. The simulation results are included in Table 6.2 and indicate that the isobutene conversion and ether purity are much lower for ETBE. The reactive distillation process provides a slight improvement in isobutene conversion (approximately 0.5% with a 5% ethanol excess) but it actually reduces the ether purity. The oxygen production rate is increased slightly as almost all the unreacted ethanol is recovered with the ether product. The net consumption of both ethanol and isobutene remain essentially unchanged.

One significant advantage arising from the reactive distillation process for ETBE is that the ethanol concentration in the distillate is reduced to 1-2 ppm. This removes any incentive to construct ethanol recovery equipment downstream of the reactive distillation column. If ethanol poisoning of a downstream catalyst is still a consideration, an additional guard bed might be required at most. Nevertheless, there is a significant reduction in processing equipment with an associated capital saving and decrease in operating expenses.

Overall, the ETBE process is probably still uncompetitive with the MTBE process due to the high ethanol consumption and the comparatively low isobutene conversion. However, the retirement of ethanol recovery equipment could provide a partial justification for the construction of an ETBE unit if the availability of capital was tight.

Table 6.2 - Reactive Distillation Processes for ETBE and MTBE (Isobutene-Rich Feed)

	<b>MTBE With 5% Excess Methanol</b>	<b>ETBE With 5% Excess Ethanol</b>	<b>ETBE With Stoichiometric Ethanol</b>
Reactor Feed Rate (kg/hr)	9,880	10,200	10,350
Overall Isobutene Conversion	<b>99.8%</b>	<b>90.5%</b>	<b>88.1%</b>
Bottoms Composition (wt%)	<b>99.3% MTBE, 0.01% MeOH, 0.7% DIB</b>	<b>91.3% ETBE, 7.1% EtOH, 1.6% DIB</b>	<b>91.8% ETBE, 6.0% EtOH, 2.3% DIB</b>
Distillate Composition (wt%)	0.06% iBut, 97.6% other C <sub>4</sub> s, 2.3% MeOH	4.9% iBut, 95.1% other C <sub>4</sub> s, 2 ppm EtOH	5.7% iBut, 94.3% other C <sub>4</sub> s, 1 ppm EtOH
Oxygen Production Rate (kg/hr)	<b>915</b>	<b>920</b>	<b>899</b>
Net Alcohol Consumption (kg/kg ether)	<b>0.365</b>	<b>0.523</b>	<b>0.512</b>
Net Isobutene Consumption (kg/kg ether)	<b>0.790</b>	<b>0.816</b>	<b>0.828</b>
Reflux Ratio	1.88	1.79	1.77
Reboiler Duty (MW)	1.58	1.40	1.43
Increase in Flooding (%)	0%	-15%	+1%

### 6.2.3.3 Advantages of Reactive Distillation

The advantages of reactive distillation for MTBE are very clear from these simulations. The isobutene conversion approaches 100% (up from around 95% for the conventional process) and the product purity is greater than 99%. These results are consistent with the current trends away from the conventional synthesis route for MTBE to processes based around reactive distillation technology. Although the second stage reaction equipment and intercooler are made redundant by the reactive distillation process, the methanol recovery equipment cannot be eliminated as there remains a significant concentration of methanol in the reactive distillation column distillate due to the various methanol-C<sub>4</sub> azeotropes present.

MTBE columns can be operated at stoichiometric methanol ratios. However, the isobutene conversion is reduced and methanol cannot be eliminated entirely from the distillate as the azeotropes continue to influence the composition of the column products. There is also no incentive to increase the ether purity as it is very high (99%+) for all methanol excesses while the volume of n-butenes is in excess of the azeotropic requirements. This allows for methanol excesses of up to around 40% for isobutene-rich feeds and much higher for isobutene-lean feeds. Even with sub-stoichiometric mixtures, methanol cannot be reacted to extinction because of a corresponding drop in conversion and the continued existence of

methanol azeotropes. As with ETBE, reducing the stoichiometric excess of methanol will result in an increase in dimerisation of isobutene to DIB.

The benefits of reactive distillation can be assessed in three main areas: raw material consumption, energy efficiency and capital cost. The relative importance of each of the areas will depend on the current refinery economics, refinery configurations, particular product specifications and other local requirements. These areas are discussed below with respect to both MTBE and ETBE synthesis.

### 1. Raw Material Consumption

Reactive distillation produces a higher overall isobutene conversion for both MTBE and ETBE (provided that some excess ethanol is used) although the increase for the ETBE process is much less significant. Isobutene conversion to ETBE is actually reduced slightly if stoichiometric ethanol is used as the benefits of internal recycling of reactants in the reactive distillation environment are partially lost. Clearly, an increased isobutene conversion reduces the net consumption of isobutene for a fixed production rate of ether.

The ether product purity remains essentially unchanged for MTBE but is decreased slightly for ETBE. Unfortunately, the decreased purity increases ethanol consumption as ethanol lost in the ether product cannot be recovered. However, ethanol is also an effective oxygenate and its presence in the ether is not necessarily detrimental. The overall fuel purity (defined as the ether concentration plus the ethanol concentration in the bottoms) is around 99% for the reactive distillation process, which is comparable to the conventional process and also MTBE production.

### 2. Energy Efficiency

No additional reboiler duty is required for reactive distillation. However, as noted above, the heat released by the reaction increases the condenser duty. This cooling duty is effectively transferred from the intercooler, which is made redundant by the process changes, but is rejected at a higher temperature (62°C at a column overhead pressure of 700 kPa compared with 40°C from the intercooler). This has process benefits with respect to heat integration and could also result in shifting cooling load from cooling-water exchangers to air coolers.



### 3. Capital Cost

Transferring the catalyst (whole or part) from the second, adiabatic, packed-bed reactor to the distillation column will incur some additional capital cost at both the fabrication and construction stages but it eliminates the intercooler and packed-bed reactor (and subsidiary equipment), with a substantially larger cost saving. There is no need to increase the column diameter for reactive distillation, provided the catalyst does not substantially change the fraction of open area present on each stage (trays or packings), as the flooding factors are similar to the non-reactive case. Additional savings can be realised from the effective elimination of ethanol from the distillate product. This is potentially a decisive advantage of reactive distillation as it removes the incentive to install ethanol recovery equipment.

Reactive distillation has clear advantages for ETBE synthesis in terms of reducing capital cost and improving energy efficiency. The advantage is less clear with respect to the increased isobutene conversion that is seen with MTBE synthesis via reactive distillation and there is, in fact, a reduction in ether purity. Overall, the benefits of reactive distillation are apparently less significant than for MTBE synthesis.

#### *6.2.3.4 ETBE-Specific Reactive Distillation Designs*

The explanation for the enhanced benefits of reactive distillation for MTBE compared with ETBE is that the chemical and phase equilibria coincide more exactly for the MTBE system. This is a necessary requirement for the successful implementation of reactive distillation. The azeotrope between methanol and various  $C_4$ s helps to lift methanol towards the reaction zone and maintains favourable reaction zone conditions. Since an equivalent azeotrope does not exist in the ETBE system, stripping separation must be optimised. If the stripping separation is too high, the reaction zone is starved of ethanol. If the stripping separation is too low, the boiling point of the ether product is suppressed by the inclusion of n-butene and other  $C_4$ s.

Operating an ETBE column with less stripping separation effectively increases the conversion at the expense of the ether purity. This case was simulated by modelling a reactive distillation column with only 12 ideal stages. The resulting column will have a significantly lower capital cost than the 30 stage column simulated previously but its ether product will contain some  $C_4$ s and will only be suitable for gasoline blending when the gasoline pool can absorb the additional light (high RVP) components. The simulation results are presented in Table 6.3 for the case with 5% stoichiometric excess of ethanol.

**Table 6.3 - ETBE-Specific Reactive Distillation Designs (Isobutene-Rich Feed)**

	<b>Low Capital Cost Process</b>	<b>High Conversion, High Purity Process</b>
Reactor Feed Rate (kg/hr)	9,760	9,320
Overall Isobutene Conversion	<b>94.6%</b>	<b>99.0%</b>
Bottoms Composition (wt%)	<b>93.8% ETBE, 5.1% EtOH, 0.8% DIB, 0.32% C<sub>4</sub>s</b>	<b>96.5% ETBE, 2.8% EtOH, 0.6% DIB, 0.06% C<sub>4</sub>s</b>
Distillate Composition (wt%)	<b>3.2% iBut, 96.6% other C<sub>4</sub>s, 0.13% EtOH, 0.08% ETBE</b>	<b>0.54% iBut, 99.1% other C<sub>4</sub>s, 0.36% EtOH, 0.04% ETBE</b>
Oxygen Production Rate (kg/hr)	<b>880</b>	<b>835</b>
Net Alcohol Consumption (kg/kg ether)	<b>0.501</b>	<b>0.478</b>
Net Isobutene Consumption (kg/kg ether)	<b>0.781</b>	<b>0.745</b>
Number of Ideal Stages	12	18
Reflux Ratio	1.98	5.0
Reboiler Duty (MW)	1.40	2.64
Column Diameter (mm)	1050	1350

Another consequence of the reduced separation in the low capital cost reactive distillation column is an increased ethanol concentration in the distillate. Under some circumstances, this may require the addition of suitable recovery equipment, negating the capital savings gained through the reduced column height. However, if the loss of ethanol in the distillate is acceptable (eg. the ethanol eventually ends up in the gasoline pool and downstream catalysts are not affected), an overall decrease in the capital cost, and increase in value added by the process, might be realised by the shorter column. The operating costs remain essentially constant as no increase in reboiler duty was specified.

Clearly, the best reactive distillation column design for ETBE synthesis would produce both a high isobutene conversion and a high ether purity. This cannot generally be realised with the same equipment used for MTBE production, unless the MTBE design was particularly serendipitous. The ideal ETBE column design produces a moderate separation but uses a high reflux ratio to continuously recycle isobutene to the reaction zone. This is not required for MTBE as the methanol azeotropes create good reaction conditions under most operating environments. The simulation results for a column with 18 ideal stages and a high reflux ratio are also shown in Table 6.3 (High Conversion, High Purity Process). Table 6.4 summarises the results from the main process alternatives (ETBE synthesis via the

conventional route, with a modified MTBE reactive distillation process and with an ideal ETBE reactive distillation process) for the case with a stoichiometric excess of ethanol.

The benefits offered by a specially designed ETBE process are significant: up to 10% higher conversion and 3-6% higher ether purity. This results in 9% lower ethanol consumption and 9% lower isobutene consumption. However, a larger diameter column (1350 mm Ø compared with 900 mm Ø for the other processes) is required and the operating costs will rise accordingly. The capital cost of the ideal ETBE column would probably be higher than the base case MTBE column, even though there are 40% less separation stages, due to the increased column diameter required. However, a very low capital cost option (Table 6.3: 12 stages, no increase in reboiler size and no recovery equipment) remains feasible. The ideal ETBE design is flexible enough to be used for MTBE production, but some reduction in performance should be anticipated (slightly reduced isobutene conversion).

**Table 6.4 - Comparison of ETBE Processes For Isobutene-Rich Feeds**

	<b>Conventional Process (Dual Reactors)</b>	<b>Modified MTBE Reactive Distillation Process</b>	<b>Ideal ETBE Reactive Distillation Process</b>
Reactor Feed Rate (kg/hr)	10,260	10,200	9,320
Overall Isobutene Conversion	<b>90.0%</b>	<b>90.5%</b>	<b>99.0%</b>
Bottoms Composition (wt%)	<b>92.5% ETBE, 6.8% EtOH, 0.7% DIB, 0.01% C<sub>4</sub>s</b>	<b>91.3% ETBE, 7.1% EtOH, 1.6% DIB, 0.01% C<sub>4</sub>s</b>	<b>96.5% ETBE, 2.8% EtOH, 0.6% DIB, 0.06% C<sub>4</sub>s</b>
Distillate Composition (wt%)	<b>5.6% iBut, 94.3% other C<sub>4</sub>s, 0.15% EtOH, nil ETBE</b>	<b>4.9% iBut, 95.1% other C<sub>4</sub>s, 2 ppm EtOH, nil ETBE</b>	<b>0.54% iBut, 99.1% other C<sub>4</sub>s, 0.36% EtOH, 0.04% ETBE</b>
Oxygen Production Rate (kg/hr)	<b>913</b>	<b>920</b>	<b>835</b>
Net Alcohol Consumption (kg/kg ether)	<b>0.526</b>	<b>0.523</b>	<b>0.478</b>
Net Isobutene Consumption (kg/kg ether)	<b>0.821</b>	<b>0.816</b>	<b>0.745</b>
Number of Ideal Stages	30	30	18
Reflux Ratio	1.20	1.79	5.0
Reboiler Duty (MW)	1.40	1.40	2.64
Column Diameter (mm)	900	900	1350

#### 6.2.4 Optimal Process for an Isobutene-Lean Feed

This section examines the implications of processing  $C_4$  hydrocarbon from a catalytic cracking unit (CCU) and, again, the effect on process selection. A typical feed composition of 15% isobutene, 35% n-butenes, 40% isobutane and 15% n-butane was assumed. Process designs were again completed for 5000 kg/hr (1000 bbl/day) etherification units using (a) conventional technology, (b) a reactive distillation column that was designed for MTBE synthesis, and (c) two designs which were specifically tailored for ETBE synthesis. As with the previous case study, Pro/II was used for all simulations. A similar set of assumptions (chemical equilibrium, reaction model of Jensen and Datta, 1995) and property packages (UNIFAC and Soave-Redlich-Kwong), were also made in modelling the various systems described here.

##### 6.2.4.1 Conventional Process

The process schematic shown in Figure 6.1 was again used as the basis for simulations of the conventional etherification process. The MTBE case with 5% excess methanol and two ETBE cases (with and without a stoichiometric excess of ethanol) were initially modelled. The results have been summarised in Table 6.5. Although the composition of the column feed varies significantly from the first case study, the same column (i.e. 30 stages) was successfully used for this case study. The main difference arises in the flow rate of the distillate product which increase substantially due to the increased presence of non-reactive  $C_4$  hydrocarbons. Consequently, a much lower reflux rate of 0.35 was specified. This results in an approximately equivalent reflux rate when compared with the isobutene-rich feed cases.

With equivalent equipment, the isobutene conversion to ETBE and the ETBE product purity are both significantly lower than found for the MTBE process when using an isobutene-lean feed. However, the differences between MTBE production and ETBE production are less than was seen for feeds that are isobutene-rich. The higher ether product purity has the unfortunate disadvantage of reducing the oxygen production rate as less ethanol is recovered with the ether product. The remaining unreacted ethanol is recovered with the distillate product (at concentrations of 2-3%) so that further processing of the distillate is required. A lower reboiler duty is required for ETBE production but there appear to be no other advantages and MTBE production would clearly be favoured on the results presented in Table 6.5, even if a cheap source of ethanol was available.

**Table 6.5 - Conventional Processes for ETBE and MTBE (Isobutene-Lean Feed)**

	<b>MTBE with 5% Excess Methanol</b>	<b>ETBE with 5% Excess Ethanol</b>	<b>ETBE with Stoichiometric Ethanol</b>
Reactor Feed Rate (kg/hr)	22,660	20,380	20,750
Second Stage Reactor Outlet Temperature (°C)	45	48	48
iBut Conversion: 1st Reaction Stage	84.0%	75.5%	73.9%
2nd Reaction Stage	64.2%	60.8%	56.3%
Overall	<b>93.6%</b>	<b>89.8%</b>	<b>88.2%</b>
Bottoms Composition (wt%)	<b>99.2% MTBE,</b> 0.01% MeOH, 0.8% DIB	<b>96.1% ETBE,</b> 3.1% EtOH, 0.7% DIB	<b>97.2% ETBE,</b> 2.1% EtOH, 0.8% DIB
Distillate Composition (wt%)	0.9% iBut, 98.0% other C <sub>4</sub> s, 1.1% MeOH	1.5% iBut, 97.3% other C <sub>4</sub> s, 1.2% EtOH	1.8% iBut, 97.1% other C <sub>4</sub> s, 1.1% EtOH
Oxygen Production Rate (kg/hr)	<b>915</b>	<b>841</b>	<b>823</b>
Net Alcohol Consumption (kg/kg ether)	<b>0.365</b>	<b>0.527</b>	<b>0.511</b>
Net Isobutene Consumption (kg/kg ether)	<b>0.680</b>	<b>0.611</b>	<b>0.623</b>
Reboiler Duty (MW)	3.07	2.80	2.84
Column Diameter (mm)	1650	1350	1350

#### 6.2.4.2 Reactive Distillation Process

As was done for the case study with an isobutene-rich feed, a reactive distillation system was designed and optimised for MTBE production. The operating conditions and key results are shown in Table 6.6. This technology again outperforms the conventional process with respect to the isobutene conversion obtained but only by around 2% whereas an increase of around 5% was seen with the isobutene-rich feed. When the same equipment was used for ETBE synthesis, the isobutene conversion was around 5% lower and the ether purity was around 7% lower. However, compared with the conventional process for ETBE synthesis, the conversion was 2-3% higher. Unfortunately, the increase in conversion was at the expense of the purity.

The reactive distillation process again offers better energy efficiency (heat of reaction liberated 22°C higher than the conventional process) and reduced capital cost, especially if the ethanol recovery equipment can be dispensed with due to the reduction in the ethanol content of the distillate product. However, reactive distillation technology still appears insufficient to make the ETBE process competitive.

**Table 6.6 - Reactive Distillation Process for ETBE and MTBE (Isobutene-Lean Feed)**

	<b>MTBE With 5% Excess Methanol</b>	<b>ETBE With 5% Excess Ethanol</b>	<b>ETBE With Stoichiometric Ethanol</b>
Reactor Feed Rate (kg/hr)	21,850	19,780	20,360
Overall Isobutene Conversion	<b>97.1%</b>	<b>92.5%</b>	<b>89.9%</b>
Bottoms Composition (wt%)	<b>99.1% MTBE, 0.0% MeOH, 0.9% DIB</b>	<b>93.0% ETBE, 6.1% EtOH, 0.9% DIB</b>	<b>93.8% ETBE, 5.1% EtOH, 1.1% DIB</b>
Distillate Composition (wt%)	0.5% iBut, 98.7% other C <sub>4</sub> s, 0.9% MeOH	1.2% iBut, 98.8% other C <sub>4</sub> s, 0.03% EtOH	1.6% iBut, 98.4% other C <sub>4</sub> s, 0.01% EtOH
Oxygen Production Rate (kg/hr)	<b>915</b>	<b>899</b>	<b>879</b>
Net Alcohol Consumption (kg/kg ether)	<b>0.365</b>	<b>0.512</b>	<b>0.502</b>
Net Isobutene Consumption (kg/kg ether)	<b>0.656</b>	<b>0.593</b>	<b>0.611</b>
Reflux Ratio	0.72	0.77	0.76
Reboiler Duty (MW)	3.07	2.80	2.84
Increase in Flooding (%)	0%	-2%	-7%

#### 6.2.4.3 ETBE-Specific Reactive Distillation Designs

As with the isobutene-rich feed cases, a reactive distillation column can again be designed with fewer separation stages to increase the isobutene conversion. Similarly, a moderate number of separation stages can be combined with a high reflux ratio to produce both a high isobutene conversion and a high ether product purity. These cases were simulated here and the results are presented in Table 6.7.

The low capital cost process increases the isobutene conversion to 95.4% (an increase of around 3% compared with ETBE production in a reactive distillation column designed for MTBE synthesis). The corresponding ether purity is also higher than the cases presented in Table 6.6. However, the most significant results are shown in the third column of Table 6.7 which shows results for a high conversion, high purity case. The isobutene conversion and ether product purity for this case are not only significantly higher than all other ETBE cases, but are higher than the those for MTBE production with this type of feed. The ethanol concentration in the distillate is high enough to require careful consideration of the need for additional recovery equipment but this process appears competitive with MTBE production.

**Table 6.7 - ETBE-Specific Reactive Distillation Designs (Isobutene-Lean Feed)**

	<b>Low Capital Cost Process</b>	<b>High Conversion, High Purity Process</b>
Reactor Feed Rate (kg/hr)	19,180	18,390
Overall Isobutene Conversion	<b>95.4%</b>	<b>99.5%</b>
Bottoms Composition (wt%)	<b>96.9% ETBE, 2.2% EtOH, 0.7% DIB, 0.22% C<sub>4</sub>s</b>	<b>99.2% ETBE, 0.18% EtOH, 0.6% DIB, &lt; 0.01% C<sub>4</sub>s</b>
Distillate Composition (wt%)	0.66% iBut, 98.5% other C <sub>4</sub> s, 0.76% EtOH, 0.11% ETBE	0.08% iBut, 99.0% other C <sub>4</sub> s, 0.87% EtOH, 1 ppm ETBE
Oxygen Production Rate (kg/hr)	<b>824</b>	<b>788</b>
Net Alcohol Consumption (kg/kg ether)	<b>0.496</b>	<b>0.476</b>
Net Isobutene Consumption (kg/kg ether)	<b>0.575</b>	<b>0.552</b>
Number of Ideal Stages	12	18
Reflux Ratio	0.81	1.50
Reboiler Duty (MW)	2.80	3.80
Column Diameter (mm)	1500	2000

Table 6.8 compares the ETBE production rates and conditions for the three systems discussed above. The benefits of a specially designed ETBE process are up to 10% higher conversion and 4% higher ether purity. This translates into 10% lower consumption of raw materials. The downside is again increased operating expenses due to the higher reflux rate, reboiler duty and internal column vapour-liquid traffic.

Interestingly, for ETBE production, the best results were obtained from a feed that was relatively lean in isobutene: 99.5% isobutene conversion and 99.2% ether purity with an 18-stage column and a high reflux ratio. For MTBE production, the reverse was applicable. The best results for MTBE were obtained with a feed that was rich in isobutene: 99.8% conversion and 99.3% purity in a 30-stage column with moderate reflux ratio. For a feed that was lean in isobutene, the conversion to MTBE was at least 2% lower than was achieved with ETBE. High MTBE conversions could have been achieved by increasing the reflux ratio in the 30 stage column, but the shorter column ETBE would still produce around 2% higher yields at the same reflux ratio.

Table 6.8 - Comparison of the ETBE Processes With Isobutene-Lean Feeds

	<b>Conventional Process (Dual Reactors)</b>	<b>Modified MTBE Reactive Distillation Process</b>	<b>Ideal ETBE Reactive Distillation Process</b>
Reactor Feed Rate (kg/hr)	23,020	22,340	20 770
Overall Isobutene Conversion	<b>89.8%</b>	<b>92.5%</b>	<b>99.5%</b>
Bottoms Composition (wt%)	<b>96.1% ETBE,</b> 3.1% EtOH, 0.7% DIB, 0.01% C <sub>4</sub> s	<b>93.0% ETBE,</b> 6.1% EtOH, 0.9% DIB, 0.01% C <sub>4</sub> s	<b>99.2% ETBE,</b> 0.18% EtOH, 0.6% DIB, < 0.01% C <sub>4</sub> s
Distillate Composition (wt%)	1.5% iBut, 97.3% other C <sub>4</sub> s, 1.2% EtOH, nil ETBE	1.2% iBut, 98.8% other C <sub>4</sub> s, 0.03% EtOH, nil ETBE	0.08% iBut, 99.0% other C <sub>4</sub> s, 0.87% EtOH, 1 ppm ETBE
Oxygen Production Rate (kg/hr)	<b>841</b>	<b>899</b>	<b>788</b>
Net Alcohol Consumption (kg/kg ether)	<b>0.527</b>	<b>0.512</b>	<b>0.476</b>
Net Isobutene Consumption (kg/kg ether)	<b>0.611</b>	<b>0.593</b>	<b>0.552</b>
Number of Ideal Stages	30	30	18
Reflux Ratio	0.35	0.77	1.50
Reboiler Duty (MW)	2.80	2.80	3.80
Column Diameter (mm)	1350	1350	2000

This result attests to the range of interactions present between chemical and phase equilibria, and the complexity of the reactive distillation design problem. For MTBE reactive columns the dilution effect of reducing the isobutene concentration in the feed predominates over the cooling effect. For ETBE columns the reverse is true. The ether manufacturer should consider such effects when deciding the type of ether unit to be built (MTBE, ETBE or another ether) and optimising its design.

#### 6.2.5 Process Comparison for ETBE Production

Reactive distillation offers substantial process benefits for both MTBE and ETBE production. The maximum isobutene conversion and ether purity for ETBE production are limited by the unfavourable reaction equilibrium, kinetics and azeotropes, when using the conventional technology. However, in a specially designed reactive column, these limitations can be overcome and conversions and purities above 99% can be achieved, matching the results attainable for MTBE production. The optimum design for ETBE columns is different to that which is commonly used for MTBE production. A shorter column and higher reflux ratio is required to optimise the reaction zone conditions and,



therefore, maximise conversion. If extensive ETBE production is anticipated, a specific ETBE column design should be developed to maximise profitability. Alternatively, if only occasional ETBE production is required, standard MTBE equipment is sufficient as an isobutene conversion and ether purity of 90%+ can still be attained.

## **6.3 PROCESS OPTIMISATION**

### **6.3.1 Requirement for Optimisation**

The benefits of reactive distillation arise from the combination of reaction and separation within a single unit operation. As indicated previously, the overall capital cost of a reactive distillation process is likely to be considerably less than a comparable two-stage flowsheet and process advantages sometimes arise from the constant recycling of reactants to the reaction zone. However, these advantages are partially offset by the increased process complexity and potential difficulties with operation and control.

The main source of difficulty is that it is desirable to simultaneously produce both a high reactant conversion and a high product purity. That is, it must duplicate both functions of the two-stage process. However, the operating conditions that maximise reactant conversion do not coincide with the conditions that maximise the product purity so that the dual objectives are not entirely compatible. In an industrial environment, the best solution to this dilemma is to continuously optimise the process according to an objective function that is based on economic considerations and is dependent on both parameters (purity and conversion).

The optimisation should be undertaken at three levels: at the primary level, an effective regulatory control system is required to stabilise the process and reject the effects of disturbances; at the secondary level, the controller set-points should be regularly updated to reflect changing production targets; and at the tertiary level, the parameters of the optimisation should be updated to reflect changes in the external economic conditions. The primary level of optimisation is discussed in some detail in the following chapters while the tertiary level is outside the scope of this work. The framework for implementing the secondary level of process optimisation is discussed here.

### 6.3.2 Optimisation Procedure and Techniques

#### 6.3.2.1 Objective Function

The objective function should reflect the net value added or profitability of the process. Table 6.9 indicates the typical value of each component in the feed, distillate and bottoms product, and also the value of energy. The values shown (in dollars per tonne) were assumed for this study and do not necessarily reflect current prices although care was taken to make the scenario realistic. With respect to the optimisation, the units and magnitudes are arbitrary (only the relative values affect the location of the optimum).

The high negative value of ethanol in the distillate reflects the potential to excessively age or poison downstream catalysts. The reduced value of C<sub>4</sub> components in the bottoms product reflect the effect on the gasoline pool volatility and the need to balance C<sub>4</sub> with higher value components to meet overall volatility specifications. The fixed operating costs do not need to be considered as these do not affect the results of the optimisation (only the magnitude of the profitability).

The overall objective function can be expressed as:

$$\text{Profitability (P)} = \text{Product Value} - \text{Feed Cost} - \text{Energy Cost} \quad (6.9)$$

Table 6.9 - Economic Scenario

<b>Feed and Product Values</b>	<b>Feed</b>	<b>Distillate</b>	<b>Bottoms</b>
Ethanol (\$/tonne)	-	-250	450
Isobutene (\$/tonne)	-	150	120
ETBE (\$/tonne)	-	0	800
Non-Reactive C <sub>4</sub> (\$/tonne)	-	150	120
Overall (\$/tonne)	250	-	-
<b>Energy Costs</b>			
Heating (\$/kW)	0.03		
Cooling (\$/kW)	0.02		

Adopting the nomenclature described below and the values from Table 6.9:

$$P = (450 x_1 + 120 x_2 + 800 x_3 + 120 x_4) B + (-250 y_1 + 150 y_2 + 150 y_4) D - 250 F - 30 Q_r - 20 Q_c \quad (6.10)$$

The net value added per unit of feed is also of interest since the production rate is likely to be determined by other factors (i.e. demand):

$$P^* = (450 x_1 + 120 x_2 + 800 x_3 + 120 x_4) B/F + (-250 y_1 + 150 y_2 + 150 y_4) D/F - 250 - 30 Q_r/F - 20 Q_c/F \quad (6.11)$$

### 6.3.2.2 Constraints

The reactive distillation column can only be operated within the constraints imposed by the equipment design. These constraints include the maximum duties of the reboiler and the condenser, the column capacity (i.e. flooding point) and the restrictions on the composition of products due to downstream processing or blending requirements. The following constraints were assumed for this example, using a consistent nomenclature:

$$Q_r < 6.00 \quad (6.12)$$

$$Q_c < UA (T_c - T_d) \quad (6.13)$$

$$\text{Vapour Flooding Factor} < 80\% \quad (6.14)$$

$$\text{Downcomer Flooding Factor} < 80\% \quad (6.15)$$

$$y_1 < 0.025 \quad (6.16)$$

$$(x_2 + x_4) < 0.020 \quad (6.17)$$

$$x_3 > 0.900 \quad (6.18)$$

A concentration of greater than 2.5% ethanol in the distillate was assumed to cause irreversible catalyst damage to a downstream unit. A total  $C_4$  concentration of greater than 2.0% in the bottoms was assumed to violate an intermediate (or final) volatility specification. A minimum ETBE purity of 90% was specified as a blending requirement.

### 6.3.2.3 Optimisation Method

Either equation (6.10) or (6.11) can be used to optimise the column's operating conditions. The primary manipulated variables (i.e. the condenser duty for the column pressure and the reboiler duty and reflux rate for the product compositions) could be optimised directly but it is preferable to find the optimal control set-points instead. These set-points can then be used within the existing control structure to reject minor disturbances in the feed rate or composition, etc. The situation is analogous to the justification for simple cascade controllers.

The multi-variable optimisation was undertaken within SpeedUp™ using a feasible-path successive quadratic programming routine (Aspen Technology, 1993). The global system of equation includes several local maxima so that the selection of the starting point was important. A starting point that corresponded to a high ETBE purity in the bottoms product was found to converge to the global optimum in all the cases examined.

### 6.3.3 Optimisation Results

#### 6.3.3.1 Steady-State Solutions

The results of the optimisation are shown in Table 6.10. Two additional optimisation runs were performed to demonstrate the incentive for considering both reaction and separation together. The maximum profitability is achieved when neither the ETBE purity nor the isobutene conversion is at its maximum. Underlined results indicate active constraints.

Table 6.10 - Optimised Process Parameters and Results.

	<i>Maximum Value Added</i>	<b>Maximum ETBE Purity</b>	<b>Maximum Conversion</b>
<b>Set-Points</b>			
Overhead Pressure (kPa)	650	725	750
Stage 7 Temperature (°C)	104	113	105
Reflux Rate (m <sup>3</sup> /hr)	17.5	21	22
<b>Key Results</b>			
ETBE Purity (wt%)	95.1	95.7	95.4
Isobutene Conversion (mol%)	94.6	95.4	95.5
Profitability (\$/m <sup>3</sup> )	1744	1730	1733
<b>Constraints</b>			
Reboiler Duty (MW)	5.10	5.64	5.73
Condenser Duty (MW)	<u>3.90</u>	4.35	4.41
Maximum Flooding Factor (%)	74	<u>80</u>	<u>80</u>
Ethanol in Distillate (wt%)	0.18	0.38	0.25
C <sub>4</sub> in Bottoms (wt%)	0.45	0.36	0.63

The profitability of the unit is limited by the maximum condenser duty. A decrease in the column pressure would increase the net value added by the process if the overhead vapour could be condensed at the lower temperature. This indicates that there is an opportunity to increase profitability by debottlenecking the condenser until one or more additional constraints become active. Interestingly, a higher ETBE purity and isobutene conversion are achievable at pressures above the optimum. The increased pressure alleviates the condenser limit but introduces a flooding limit.

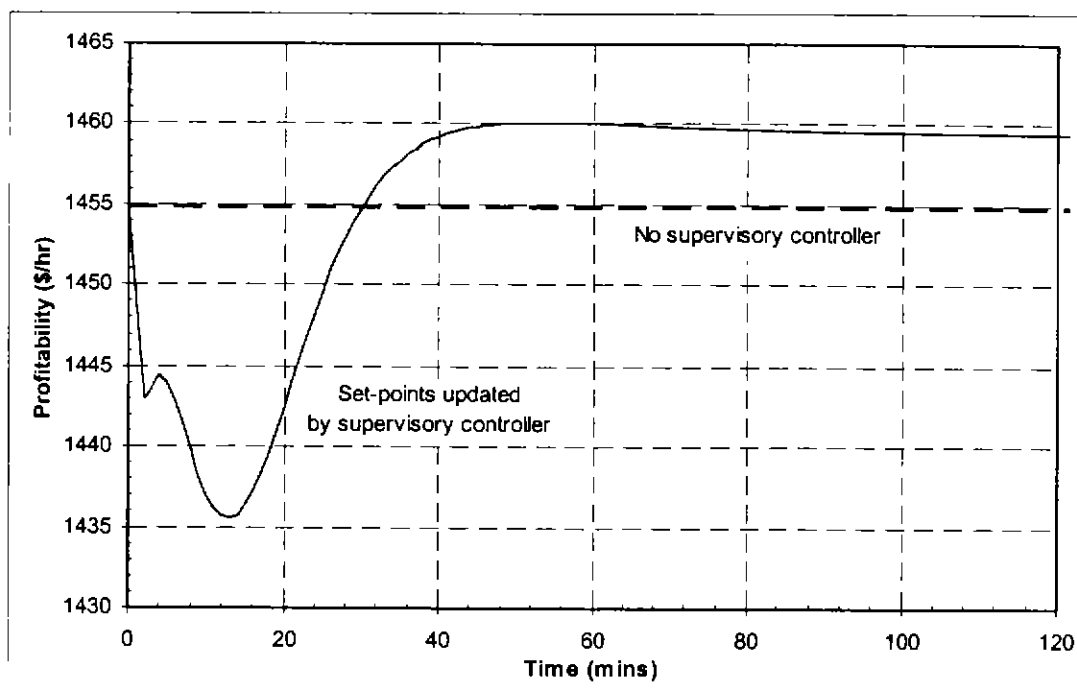
It is pertinent to examine the unconstrained extrema (i.e. peak values without constraints) in this system. The maximum unconstrained profitability of \$1750/hr is achieved at a pressure

of 500 kPag. At lower pressures, the departure from chemical equilibrium increases due to the slower reaction rate and the maximum conversion (and consequently the maximum purity also) decrease. The maximum unconstrained ETBE purity is 97.3% and occurs at very high internal vapour and liquid rates. The profitability at this point is only \$1470/hr due to the excessive use of utilities. There is no maximum unconstrained isobutene conversion as increasing the reflux rate (and adjusting the other parameters appropriately) *always* increases the conversion.

#### 6.3.3.2 Supervisory Control System

The results of this process optimisation can be used within a supervisory control system. This is shown in Figure 6.5 which considers the dynamic response to set-point changes implemented by a supervisory controller following a process disturbance. In this case, the disturbance was assumed to be a decrease in the feed rate from 120 kmol/hr to 100 kmol/hr. Initially, the column is operating with the optimal set-points and, therefore, maximum profitability. The column is allowed to stabilise at the new feed rate before time = 0 in Figure 6.5. Thus, the set-points are now sub-optimal and the column is operating below peak profitability.

The supervisory controller calculates new set-points by optimising the column operation at the new conditions. These set-point changes are implemented at time = 0 in Figure 6.5 and have an immediate destabilising effect on the column. Initially, this reduces the profitability but after the process transient is completed, the profitability has been increased. The net economic benefit of employing the supervisory control system is equivalent to the area between the solid line (supervisory control system implemented) and the dashed line (set-points not updated after disturbance). After less than two hours, the initial lost production has been recovered and, thereafter, the supervisory controller makes a net profit.



**Figure 6.5 - Process Response to a Feed Rate Disturbance: Benefits of Supervisory Control**

The supervisory controller can also be used to optimise the process performance following feed composition changes. However, steady-state simulations show that there is little incentive to manipulate the process set-points in response to feed composition changes: the net benefit is less than \$1/hr for compositions in the practical interval around the base case. This is convenient as it is far more difficult to implement a supervisory control system which must reflect compositional changes as well as rate changes. Process analysts are required to measure compositions and these introduce an extra cost and process dead time. This dead time reduces the process controllability and results in a more sluggish response to disturbances. Consequently, the viability of the compositional aspect of a supervisory controller is questionable.

#### **6.3.4 Effectiveness of Process Optimisation**

The effectiveness of a supervisory control system for this column is strongly dependent on two factors: the accuracy of the process model used for the optimisation; and the controller tunings. Plant-model mismatch can result in non-optimal changes so that there is no increase in profitability even after the process transient is complete. Regular feedback from the actual process, including data reconciliation, is required to ensure that the plant-model mismatch is minimised. Aggressive controller tunings are also required to minimise the effect of making set-point changes. Poorly tuned controllers result in large production losses before the new optimal conditions are attained. On the other hand, tightly tuned

controllers allow more regular updating of set-points and, therefore, increase the economic benefit of the supervisory system.

The benefits of reactive distillation for the synthesis of fuel ethers such as ETBE have been clearly demonstrated but the dual process objectives, which are inherent in the combination of reaction and separation, require a careful rationalisation of operating conditions in order to maximise profitability. A satisfactory process optimisation can only be achieved by considering the net values and costs of both distillation products, the feed and utilities consumption, and the influence of process equipment constraints.

Although the optimum conditions for maximum profitability in a reactive ETBE column do not coincide with either maximum product purity or maximum reactant conversion, it is possible to implement a supervisory control system based on a relatively simple optimisation framework. It was shown, using dynamic simulations, that a supervisory control system could be used to increase the net profitability of a column by ensuring that the regulatory control system set-points were reset to their optimum values following process disturbances.

## **6.4 OVERALL SUMMARY OF FINDINGS ON DESIGN ISSUES**

The discussions and investigations presented in Chapters 3-6 were motivated by a lack of understanding of many practical aspects of hybrid reactive distillation design. It was shown that a reactive distillation simulation model could be built using the equilibrium stage model with appropriate modifications to reflect the reaction(s), and that this model accurately predicted the operating conditions and product compositions of an actual MTBE column that was used to validate the modelling process. The model can be modified to simulate both equilibrium reactions and kinetically controlled reactions so that it provides a satisfactory basis for the analysis of the operating characteristics of hybrid reactive distillation and for design studies.

The full hybrid reactive distillation model was used to simulate several ETBE and MTBE columns to determine the effect of key process variables. These effects have not previously been documented and were shown to vary significantly from what would be expected in a conventional distillation column. For example, the operating pressure of a reactive column should be optimised to balance the reaction and separation functions of the system. In addition to the readily apparent effects of pressure on the reaction equilibrium and rate constants (via changes in the phase equilibrium temperature) and on the relative volatility,

the operating pressure affects the stage-to-stage compositions in a manner which can influence the direction and extent of the reaction.

It was also found that increasing fractionation is sometimes detrimental for the reaction and that the highest product purity and reactant conversion in a hybrid column are obtained with an intermediate number of stages and high reflux ratio. It is often not possible to match the effects of reflux with additional stages as can be done with non-reactive distillation.

There is an absence of suitable design methods for hybrid reactive distillation in the literature. However, residue curves diagrams and reactive residue curves diagrams can be used to indicate the feasibility of a reaction-separation and provide useful *a priori* information regarding the internal column compositions. Rigorous simulations can then be used to optimise the operating conditions and column topography and to perform the detailed design. A design strategy was proposed to assist this process.

The integration of hybrid reactive distillation technology within a process plant was also considered. It was found that ETBE could be a more attractive synthesis than MTBE (despite less favourable reaction thermodynamics) where the hydrocarbon feed was lean in isobutene. It was also found that the choice of ETBE production (rather than MTBE production) could sometimes result in a significantly lower capital outlay as some recovery equipment might be made redundant. The optimisation of an integrated ETBE process was then considered and the target operating conditions (i.e. control system set-points) were determined from a set of assumed economic constraints.



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## CHAPTER SEVEN

### DYNAMIC SIMULATION

- 7.1 Problem Formulation**
- 7.2 Reactive Distillation Dynamic Model**
  - 7.2.1 Column Configuration, Modelling Assumptions and Simulation Package
  - 7.2.2 Reactive Stage Model
  - 7.2.3 Non-Reactive Stage Model
  - 7.2.4 Feed Stage Model
  - 7.2.5 Condenser Model
  - 7.2.6 Reboiler Model
- 7.3 Steady State Solution of the Dynamic Model**
- 7.4 Process Dynamics and Transient Responses**
  - 7.4.1 Open Loop Transients
    - 7.4.1.1 Step Change in Feed Rate
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  - 7.4.2 Other Transient Responses
    - 7.4.2.1 Catalyst Ageing
    - 7.4.2.2 Ambient Temperature Rise

#### 7.1 PROBLEM FORMULATION

The equations used to model a dynamic process form a set of differential algebraic equations (DAEs). The numerical solution of these equations requires them to be reduced to a matrix of algebraic equations (AEs) and ordinary differential equations (ODEs). The number of differentiation steps required to complete this task is referred to as the index of the problem. Numerical solution methods are now available for systems of equations with an index greater than one (i.e. high index problems) but these methods are significantly more complex to implement and are not presently included in most commercial dynamic simulators. Therefore, it is crucial to formulate problems to be of index of zero or one, wherever possible.

The index of a problem is determined by the structure of the equations *and* the boundary conditions specified. A valid set of equations (derived from correct and consistent mass and energy balances and valid assumptions about the process) and boundary conditions can still result in a problem with index greater than one. Although a dynamic solution might not be

available, high index problems can often readily be solved in the steady state using conventional algorithms.

The problem index is not immediately apparent before solution commences and the determination of the index is, itself, a difficult task where many equations are present (e.g. the model of a basic distillation column with several stages might contain over 1000 equations). Corollaries to this observation are that the cause of a high index problem is often difficult to ascertain and that a method for remedying an index problem might not be readily available. There has been speculation on the causes of high index problems (e.g. Gani and Cameron, 1992; Unger et al., 1995) and practical approaches to overcoming this impediment where the number of equations prevents a detailed matrix analysis have only recently become available.

Distillation processes have been shown to be particularly susceptible to index problems in the solution of the global set of DAEs (Ponton and Gawthrop, 1991; Unger et al., 1994). An important precaution in avoiding such a problem is to ensure that the overall model must be fully closed (Moe et al., 1995). This requires that algebraic relationships exist between the constitutive equations, balance equations and rate equations. In practice, this requires elaboration of the relationships between stage-to-stage pressure drop, stage-to-stage hold-up and vapour and liquid internal flows.

The potential for index in reactive distillation appears to be even higher (due to the influence of the reaction) and there have been several claims that the formulation of a problem with an index less than two is not possible for a system in both phase and chemical equilibrium using conventional methods (e.g. Moe et al., 1995; Perez-Cisneros et al., 1996). A transformation for the composition co-ordinates has been recommended (Barbosa and Doherty, 1992; Perez-Cisneros et al., 1996) as a means for circumventing the index problem by making the concentration variables independent of the extent of reaction but it has not been demonstrated that this is necessary.

Despite the absence of lucid direction in the literature, some general conclusions can be drawn about modelling techniques that can lead to high index problems:

- invalid assumptions can lead to equations where one variable or set of variables in the system of ODEs is independent of a particular state variable, resulting in an ODE matrix with a rank deficiency (a sign of high index);
- modelling one parameter in two different ways can produce an equation in the ODE matrix with no unknowns, even if the overall degrees of freedom constraint

is satisfied;

- the choice of the set variables (boundary conditions) can sometimes transform a consistent set of equations into a higher index problem (examples of this have been shown by Gani and Cameron, 1992 and Unger et al., 1995);
- models must be closed so that balance equations, constitutive equations and rate equations are all related (Moe et al., 1995).

With respect to distillation and reactive distillation, some further considerations are applicable for dynamic simulation problems (but not necessarily for steady state simulations):

- no state variable can be set arbitrarily at a constant value (e.g. overhead pressure);
- simplifying assumptions for pressure drop (e.g. constant pressure drop for each stage, independent of vapour or liquid flow rates) and hold-up (eg. constant volume per stage, independent of liquid flow) are *not* valid for dynamic simulations;
- equilibrium stage equations are generally straight forward to define but *must* include relationships for pressure drop and hold-up to 'close' the model;
- condenser and reboiler configurations and boundary conditions are critical - small and apparently insignificant changes can be sufficient to change the index of a problem.

As the problem index is dependent on both the equations structure and the boundary conditions (set variables), high index problems are still possible with a fully 'closed' model. However, by adding extra variable relationships and replacing variables with constants where possible, the number of variables to be specified can be limited to the feed conditions and the fundamental degrees of freedom for operation. This reduces the likelihood of an illegal combination and an index problem arising from boundary conditions.

An index problem can also arise from the linking of models whose individual indices are zero or one. This results from the formation of equation groups that are linked in a cyclic arrangement by, for example, pressure drop relationships. It is possible to create a situation where the pressure at one point (usually the reboiler or condenser) is overspecified while the pressure at another point is essentially independent of feed streams to that stage.

There are certainly pitfalls in the problem formulation but a dynamic reactive distillation model of index one can be produced without employing any numerical tricks or internal

variable transformations. Such a model is described below in section 7.2 and implemented for the ETBE column described in Chapter 3.

## **7.2 REACTIVE DISTILLATION DYNAMIC MODEL**

### **7.2.1 Column Configuration, Modelling Assumptions and Simulation Package**

The ETBE column described in Chapter 3 (a total of 10 ideal stages) was used as the basis for the dynamic model presented here although the individual models (as described in Sections 7.2.2-7.2.6) can be combined in other ways to simulate any other column configuration.

The steady state model of the reactive distillation process used a modified set of MESH equations. This technique was retained in the dynamic model although several simplifying assumptions were added to offset the additional complexity required in the dynamic case.

The following assumptions were introduced:

- chemical equilibrium is attained on all reactive stages;
- DIB formation is negligible;
- all stages are at their bubble point so that the temperature is a function of composition only;
- ideal vapour phase.

The assumption of chemical equilibrium allows the reaction kinetics to be neglected, simplifying the modelling of the reactive stages. Negligible DIB formation allows the number of components to be reduced from five to four and the elimination of equations describing the DIB reaction. The bubble point assumption effectively permits the enthalpy derivatives to be excluded from the model - a common assumption in both simple and rigorous distillation simulation. Finally, an ideal vapour phase allows fugacity coefficients to be neglected. These assumptions slightly reduce the absolute accuracy of the model but make it a more effective dynamic simulation tool by improving the ratio of real time to simulation time.

The various physical property routines that were used are indicated in Table 7.1 and are identical to those used for steady state simulation. A recently published reaction equilibrium expression, specifically derived for ETBE, was used (Jensen and Datta, 1995) in preference to older information or equations based on MTBE synthesis. Similarly, the latest vapour pressure data was used (Krahenbühl and Gmehling, 1994).

Table 7.1 - Physical Property Routines and Sources

Property	Method and Source
Reaction equilibrium	Activities (Jensen and Datta, 1995)
Vapour pressures	Antoine equations (Krahenbühl and Gmehling, 1994)
Liquid activity coefficients	UNIFAC model
Vapour fugacity coefficients	Ideal vapour phase
Enthalpy	Soave-Redlich-Kwong equation of state
Density	Soave-Redlich-Kwong equation of state

The SpeedUp simulation environment was used to implement the full dynamic model. SpeedUp provides both the flexibility and computational power required for this task.

### 7.2.2 Reactive Stage Model

The steady state model from Section 3.2.2 must be modified to allow material accumulation and to show the relationship between the state parameters with time. This was done by considering the derivative of the molar hold-up on each equilibrium stage. Although this fundamental change is sufficient to create a time-variant model of the reactive distillation process, the resulting model would be impractical as the set of DAEs would not be solvable with available techniques. Additional equations are required to close the problem. Many formulations of these equations are possible, but a combination was selected which promotes integration with other stage models so that the global set of DAEs was also solvable.

The complete set of dynamic equations is given as equations (7.1)-(7.14), below. As with the steady state model, the heat of reaction is calculated implicitly and does not need to be separately specified. The additional equations required for model closure are equations (7.13) and (7.14). The parameters of these equations were selected empirically to restrict the extent of accumulation on each stage. Fully rigorous equations are available but the parameters do not alter the steady state problem solution and only have a minor affect on the system dynamics and, therefore, contribute unnecessarily to the complexity of the model. Equation (7.13) relates directly to the physical dimensions of the equipment being simulated. The relevant parameters were based on a pilot scale laboratory system to allow the model to be tested against experimental data.

$$\frac{dM}{dt} = L_{in} + V_{in} - L_{out} - V_{out} + \sum r_i \quad (7.1)$$

$$r_{ETBE} = -r_{EtOH} = -r_{But} \quad (7.2, 7.3)$$

$$r_{nBut} = 0 \quad (7.4)$$

$$K_{eq} = \frac{a_{ETBE}}{a_{EtOH} a_{But}} \quad (7.5)$$

$$\ln K_{eq} = 10.387 + \frac{4060.59}{T} - 2.89055 \ln T - 0.0191544T + 5.28586 \times 10^{-5} T^2 - 5.32977 \times 10^{-8} T^3 \quad (7.6)$$

$$\frac{d(Mx_i)}{dt} = L_{in}x_{i,in} + V_{in}x_{i,in} - L_{out}x_{i,out} - V_{out}x_{i,out} + r_i \quad (7.7)$$

$$\frac{d(MH)}{dt} = L_{in}H_{i,in}^L + V_{in}H_{i,in}^V - L_{out}H_{i,out}^L - V_{out}H_{i,out}^V \quad (7.8)$$

$$\frac{dH}{dt} = 0 \quad (7.9)$$

$$P \cdot y_i = \gamma_i \cdot x_i \cdot P_i^{vap} \quad (7.10)$$

$$T^V = T^L \quad (7.11)$$

$$\sum y_i = 1 \quad (7.12)$$

$$M = f(L, \rho, h, A) \quad (7.13)$$

$$P = P_{in}^V + f(M, V) \quad (7.14)$$

### 7.2.3 Non-Reactive Stage Model

The steady state model of a non-reactive stage (Section 3.2.3) requires similar alterations to those described above for the reactive stage model:

$$\frac{dM}{dt} = L_{in} + V_{in} - L_{out} - V_{out} \quad (7.15)$$

$$\frac{d(Mx_i)}{dt} = L_{in}x_{i,in} + V_{in}x_{i,in} - L_{out}x_{i,out} - V_{out}x_{i,out} \quad (7.16)$$

$$\frac{d(MH)}{dt} = L_{in}H_{i,in}^L + V_{in}H_{i,in}^V - L_{out}H_{i,out}^L - V_{out}H_{i,out}^V \quad (7.17)$$

$$\frac{dH}{dt} = 0 \quad (7.18)$$

$$P \cdot y_i = \gamma_i \cdot x_i \cdot P_i^{vap} \quad (7.19)$$

$$T^V = T^L \quad (7.20)$$

$$\sum y_i = 1 \quad (7.21)$$

$$M = f(L, \rho, h, A) \quad (7.22)$$

$$P = P_{in}^v + f(M, V) \quad (7.23)$$

#### 7.2.4 Feed Stage Model

The non-reactive stage model forms the basis of the feed stage model. Additional terms are required in the mass and energy balances to model the incoming feed:

$$\frac{dM}{dt} = L_{in} + V_{in} - L_{out} - V_{out} \quad (7.24)$$

$$\frac{d(Mx_i)}{dt} = L_{in}x_{i,in} + V_{in}x_{i,in} - L_{out}x_{i,out} - V_{out}x_{i,out} \quad (7.25)$$

$$\frac{d(MH)}{dt} = L_{in}H_{i,in}^L + V_{in}H_{i,in}^V - L_{out}H_{i,out}^L - V_{out}H_{i,out}^V \quad (7.26)$$

$$\frac{dH}{dt} = 0 \quad (7.27)$$

$$P \cdot y_i = \gamma_i \cdot x_i \cdot P_i^{vap} \quad (7.28)$$

$$T^v = T^L \quad (7.29)$$

$$\sum y_i = 1 \quad (7.30)$$

$$M = f(L, \rho, h, A) \quad (7.31)$$

$$P = P_{in}^v + f(M, V) \quad (7.32)$$

#### 7.2.5 Condenser Model

The condenser model (equations 7.33-7.39) is somewhat simpler than the non-reactive stage model although similar variable relationships are used. The condensing pressure is determined from the inlet pressure and a pressure loss which is a function of the inlet vapour flow rate only. However, it is possible to specify the condensing pressure within the global model as any pressure specification satisfies the degrees-of-freedom of the model and the index constraint.

$$\frac{dM}{dt} = V - L \quad (7.33)$$

$$\frac{d(Mx_i)}{dt} = V y_i - L x_i \quad (7.34)$$

$$\frac{d(MH)}{dt} = V H^v - L H^L - Q_c \quad (7.35)$$



$$\frac{dH}{dt} = 0 \quad (7.36)$$

$$P = \sum \gamma_i \cdot y_i \cdot P_i^{vap} \quad (7.37)$$

$$M = f(L, p, h, A) \quad (7.38)$$

$$P = P_{in}^v + f(V^2) \quad (7.39)$$

### 7.2.6 Reboiler Model

Equations (7.40)-(7.47) describe the dynamic equilibrium stage model which was used to model the partial reboiler in the reactive distillation system. The most important aspect of this model is that the stage pressure is determined implicitly from other models or fixed as a boundary condition. There are no equations relating the reboiler pressure to other pressures within the column. This distinction is required to prevent the formation of a subsystem of equations that yields a dependent equation. A dependent equation requires another variable relationship to be defined and it is suggested that this cannot be done without increasing the problem index above one.

The material hold-up in the reboiler sump is likely to be much larger than the other equilibrium stages in the column (unless a large reflux accumulator is specified) and subject to different forces. Consequently, the hold-up function (equation 7.47) should be expressed differently although this is not essential for the integrity of the global model. The Francis weir formula was used here and is recommended to relate the liquid outflow to the hold-up.

$$\frac{dM}{dt} = L_{in} - L_{out} - V_i \quad (7.40)$$

$$\frac{d(Mx_i)}{dt} = L_{in}x_{i,in} - L_{out}x_{i,out} - V y_i \quad (7.41)$$

$$\frac{d(MH)}{dt} = L_{in}H_{in}^L - L_{out}H_{out}^L - V H^v + Q_r \quad (7.42)$$

$$\frac{dH}{dt} = 0 \quad (7.43)$$

$$P \cdot y_i = \gamma_i \cdot x_i \cdot P_i^{vap} \quad (7.44)$$

$$T^v = T^L \quad (7.45)$$

$$\sum y_i = 1 \quad (7.46)$$

$$M = f(L, p, h, A) \quad (7.47)$$

### 7.3 STEADY STATE SOLUTION OF THE DYNAMIC MODEL

The global system of DAEs for the simplified dynamic model of the 10 stage reactive distillation column (Figure 3.1) comprises 568 algebraic variables and 505 linear and non-linear equations. By comparison, the full steady state model (with five components but excluding equations for dynamics, stage-to-stage pressure drops, etc.) contained 578 variables and 504 equations.

The feed conditions and column configuration that was specified in Chapter 3 for steady state simulations (see Table 3.4) were used again here. The results obtained from the simplified dynamic model (which includes several simplifying assumptions) are compared with the previous results from the full steady state model in Table 7.1. The two sets of results are almost identical and validate the use of simplifying assumptions in the dynamic model. Probably the most significant shortcomings of the dynamic model is its inability to estimate the extent of DIB formation or identify transient effects on the side-reaction rate. However, the model remains valid for most simulation studies and could be readily extended to model the side-reaction but only with a penalty to the ratio of real time to simulation time.

Table 7.1 - Comparison of Steady State and Dynamic Model Simulation Outputs

Property	Steady State Model	Dynamic Model
Condenser Temperature (°C)	79	79
Reaction Zone Temperatures (°C)	80 - 84	80 - 84
Reboiler Temperature (°C)	160	160
Isobutene Conversion (mol%)	97.5	97.7
Bottoms Composition (wt%)	96.5% ETBE, 2.7% ethanol, 0.7% butenes, 0.04% DIB	96.6% ETBE, 2.6% ethanol, 0.8% butenes
Distillate Composition (wt%)	97.7% n-butenes, 1.6% isobutene, 0.7% ethanol	97.8% n-butenes, 1.5% isobutene, 0.7% ethanol
Condenser Duty (kW)	6.73	6.71
Reboiler Duty (kW)	7.33	7.31
Reaction Rates (mol/min)	0.18 (stage 3), 0.19 (stage 4), 0.11 (stage 5)	0.17 (stage 3), 0.18 (stage 4), 0.13 (stage 5)

## 7.4 PROCESS DYNAMICS AND TRANSIENT RESPONSES

### 7.4.1 Open Loop Transients

It is becoming increasingly important to consider dynamic responses in the design phase of major engineering projects to realise the benefits of integrating control system design with process design. Process control considerations can influence equipment requirements (especially instrumentation) and can, in exceptional cases, negate the effectiveness of a design that is satisfactory at steady state but difficult to control. This is particularly true for processes such as MTBE and ETBE reactive distillation, where instability and hysteresis effects may be present (e.g. Jacobs and Krishna, 1993; Nijhuis et al., 1993).

#### 7.4.1.1 Step Change in Feed Rate

The open loop transient response to a 5% increase in feed rate with pressure, reboiler duty and reflux rate held constant is shown in Figure 7.1. Without an increase in heat input, there was a significant increase in the bottoms flow rate as the extra feed material left the column almost entirely with the ether product. The composition of the bottom product shifted to include the additional light material and the temperature decreased accordingly as the

reboiler remained in phase equilibrium. Less ethanol was returned to the reaction zone that subsequently reduced the isobutene conversion.

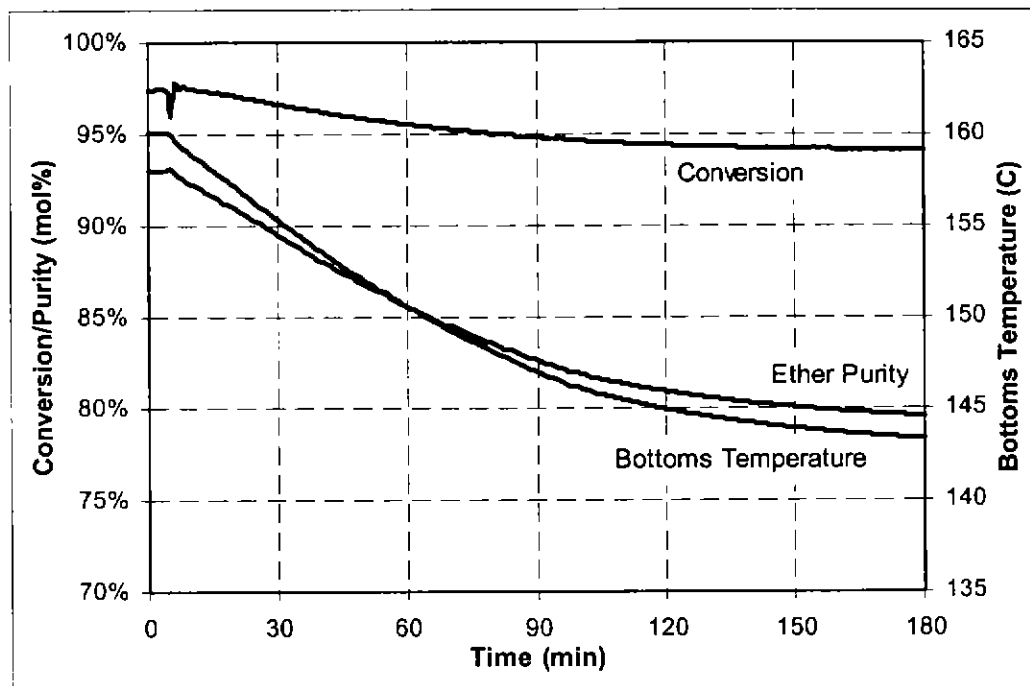


Figure 7.1 - Open Loop Response to a Step Increase in the Feed Rate

#### 7.4.1.2 Step Change in Feed Composition

Figure 7.2 shows the transient response of the same column after the feed composition was adjusted to increase the ratio of ethanol to isobutene by 2%. The total molar feed rate was fixed as were the pressure, reboiler duty and reflux rate. The responses were essentially first order under this scenario and the permanent responses became fully evident after about 40 minutes. The isobutene conversion increased slightly by the additional driving force for the reaction but ether purity decreased as the ethanol content of the bottoms product increased without additional heat input. The bottoms temperature followed the composition changes as phase equilibrium was maintained.

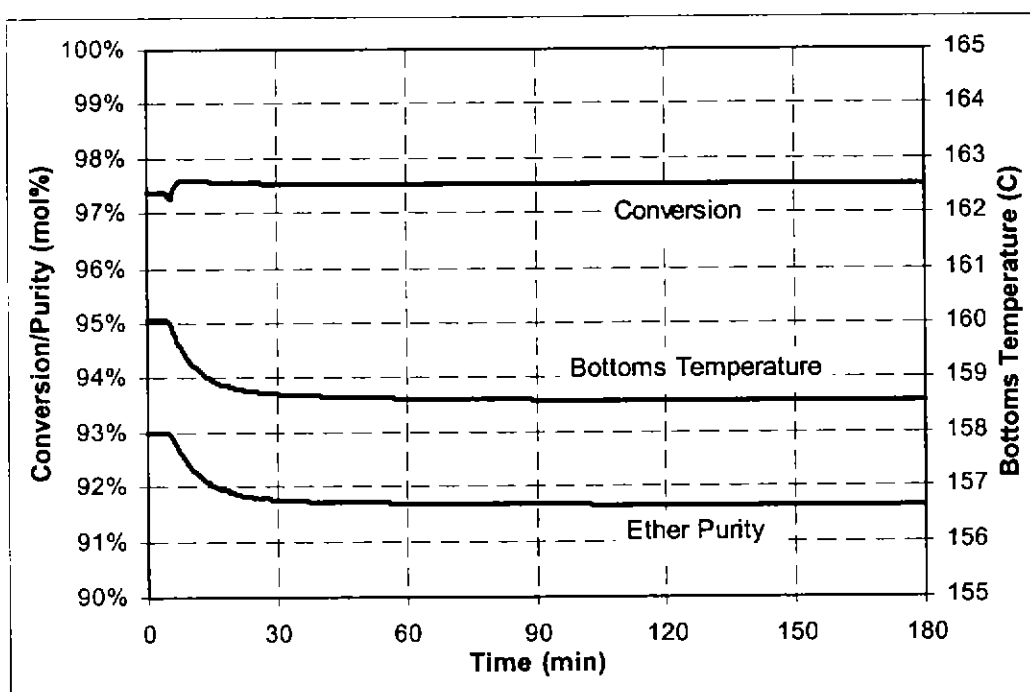


Figure 7.2 - Open Loop Response to a Step Change in the Feed Composition

#### 7.4.1.3 Step Change in Reflux Rate

The transient response to a 5% increase in reflux rate is shown in Figure 7.3. The same column was used and pressure and reboiler duty were again held constant. The initial transient was fast but only visible before the permanent changes were asserted. Without an increase in reboiler duty, the column was effectively quenched by the extra reflux and ethanol was shifted to the reboiler. The temporary increase in separation efficiency in the rectification section (due to increased vapour and liquid flows) reduced the amount of ethanol lost in the distillate and had a very short positive effect on the overall conversion. However, this effect was quickly overshadowed by the loss of ethanol from the reaction zone. Both conversion and ether purity moved quickly away from acceptable values indicating the importance of maintaining the reboiler duty close to the optimum. Changes in the distillate product became evident more quickly than in the bottoms product, indicating the damping effect of column hold-up.

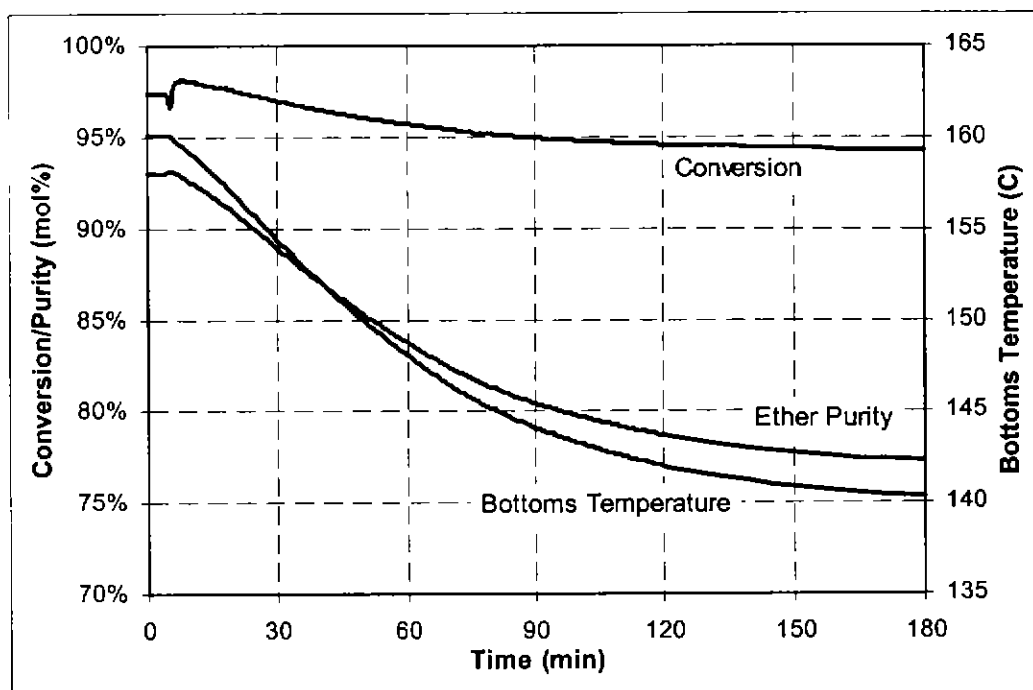


Figure 7.3 - Open Loop Response to a Step Increase in the Reflux Rate

#### 7.4.2 Other Transient Responses

The basic dynamic model was modified to simulate two other disturbances to the reactive distillation system. Firstly, catalyst ageing was simulated by re-extending the model to incorporate reaction kinetics and decreasing the amount of active catalyst present according to a simple ramp function. Secondly, changing ambient temperature was simulated by modifying the reflux rate according to a pattern that might result if an air cooler operated at its duty limit with a control configuration that manipulated the reflux drum level with the condenser duty.

##### 7.4.2.1 Catalyst Ageing

Amberlyst 15™ is susceptible to both short term poisoning and long term deactivation. A time frame of 15 hours was assumed here for the amount of active catalyst to linearly decrease to 10% of the initial catalyst load,  $m_{cat}$  (equivalent to 1% deactivation every 10 minutes), to simulate severe short term poisoning. The initial catalyst load was estimated based on the dimensions of the pilot scale column.

The full reaction rate equation, proposed for conditions where the ethanol concentration is below 4.0 mol% (Jensen, 1996), was used to provide the required kinetic information. However, the ethanol adsorption equilibrium constant ( $K_A$ ) was assumed to be constant over the reaction zone temperatures to reduce the total number of equations to be solved. The

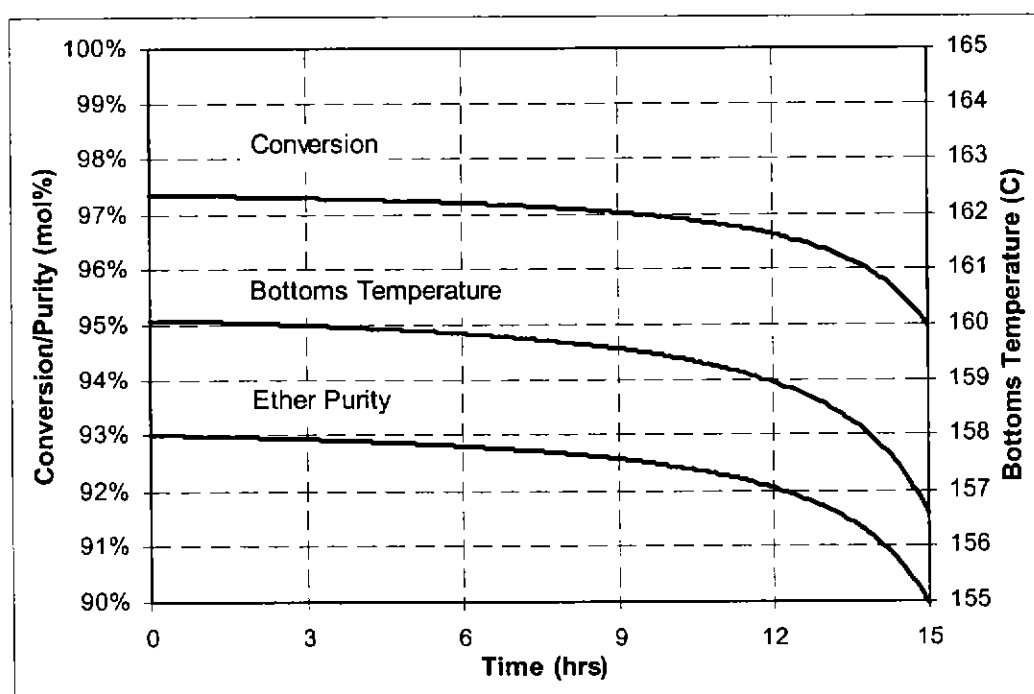
additional equations, given below, replace equation 7.5 in the basic dynamic model (equations 7.1-7.47).

$$r_{ETBE} = \frac{m_{cat} \cdot k_{rate} \cdot a_{EtOH}^2 \left( a_{iBuI} - \frac{a_{ETBE}}{K_{eq} \cdot a_{EtOH}} \right)}{(1 + K_A \cdot a_{EtOH})^3} \quad (7.48)$$

$$k_{rate} = 7.418 \times 10^{12} \exp\left(-\frac{60.4}{RT}\right) \quad (7.49)$$

$$K_A = 15 \quad (7.50)$$

Figure 7.4 shows the column response. Until the amount of active catalyst falls to around 20% of the starting load, the reductions in conversion and product purity are only slight and would probably go undetected in an industrial environment. However, after that point the effects become more exaggerated and would necessitate a unit shutdown after only a few more hours if the poisoning was allowed to continue unabated. Longer term catalyst ageing (deactivation) would probably follow a similar path on a different time scale.



**Figure 7.4 - Transient Response to Catalyst Ageing**

#### *7.4.2.2 Ambient Temperature Rise*

The reflux rate was varied in a sinusoidal pattern over a period of six hours (with a minimum of 80% of the initial value after three hours, corresponding to the daily maximum temperature) to simulate an ambient temperature rise in the morning followed by a temperature fall in the afternoon. The initial and final conditions are equivalent to the steady state described by Table 7.1. The reboiler duty was constant throughout the simulation.

This scenario corresponds to a process where the reflux drum level is controlled by manipulating the condenser duty, and the condenser is directly and strongly affected by ambient conditions (e.g. an air cooler operating at its maximum speed). In practice, the reflux drum would essentially run dry and the reflux flow control valve would saturate during periods of high ambient temperature, causing the reflux rate to fall as the ambient temperature rises. The simulation output reflects the changes to operation that would occur if the reboiler duty was not manipulated to compensate for the fall in reflux rate.

The column response to the change in reflux is shown in Figure 7.5. The changes are dramatic and clearly show the need to constantly monitor and adjust the reboiler duty to maintain acceptable operating conditions following a loss of condenser duty. The hiccup in the response that occurs between 80 and 90 minutes after the start of the simulation appears to be a result of the column readjusting itself to the relatively fast changes that occurred. The reaction conditions are temporarily stabilised due to interactions between the changing composition and reaction equilibrium. The shape of the response was not affected by rounding errors in the simulation. The response is not symmetrical due to the lags and dynamics present in the system.



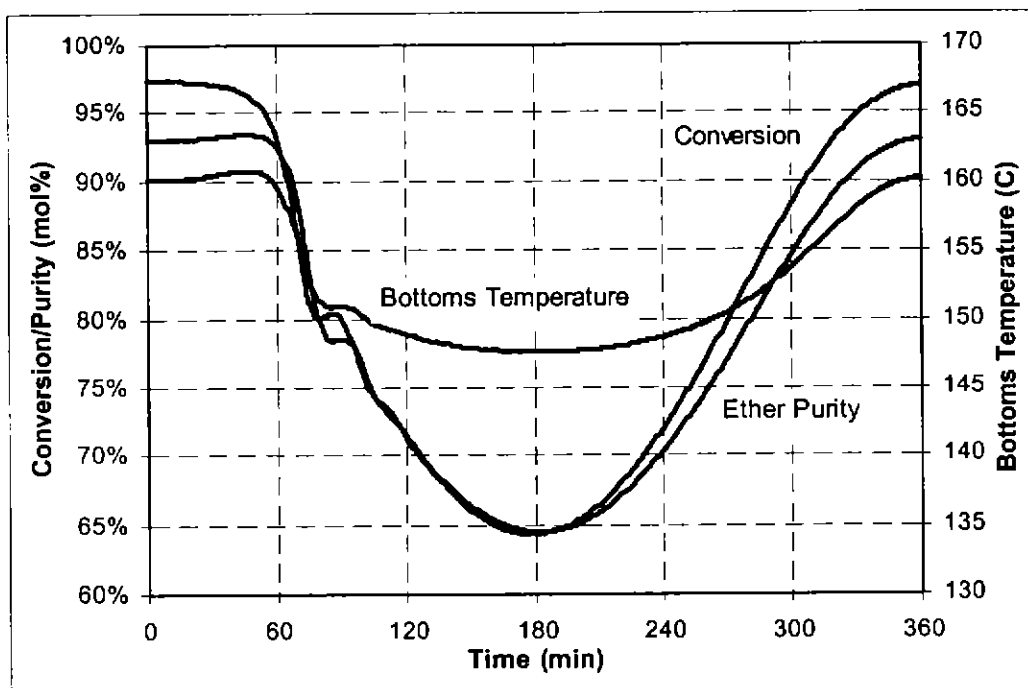


Figure 7.5 - Transient Response to Variation in Ambient Temperature

## CHAPTER EIGHT MULTIPLICITY

- 8.1 Input Multiplicity**
  - 8.1.1 General Definitions
  - 8.1.2 Examples of Input Multiplicity
  - 8.1.3 Causes of Input Multiplicity
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### 8.1 INPUT MULTIPLICITY

#### 8.1.1 General Definitions

Multiplicity refers to the condition where a one-to-one relationship does not exist between the inputs and outputs of a process. Input multiplicity is present when two or more values of an input variable produce the same output condition with all other members of the set of input variables the same. That is, the process inputs are not unique for a known output condition. Output multiplicity occurs when one complete set (i.e. a set with sufficient members to fully satisfy the degrees of freedom in the system) of input variables maps to two or more distinct and independent sets of output variables. That is, the outputs are not unique for a given set of inputs. Figure 8.1 provides a graphical distinction between input

and output multiplicity for arbitrary variables. Input multiplicity is present in the first chart as input variable values of both  $a$  and  $b$  result in the same value of the output variable. Output multiplicity is present in the second case as an input value of  $c$  could result in output values of either  $d$  or  $e$ .

The differentiation between input and output variables is best made with reference to control structures. Input variables are those which can be manipulated by controllers. The primary input variables for distillation include the reflux rate and the reboiler duty (or boilup), and the distillate and the bottoms rates, and combinations of these (e.g. the reflux ratio). The product draw rates can be considered as inputs because the inventory (level) controllers on the reflux accumulator and the reboiler sump will transmit changes in the product rates directly to the column. Output variables are those which are either controlled or used to describe the conditions of the process (e.g. product or stage temperatures, concentrations and yields). By convention, input variables are plotted on the x-axis while output variables are plotted on the y-axis.

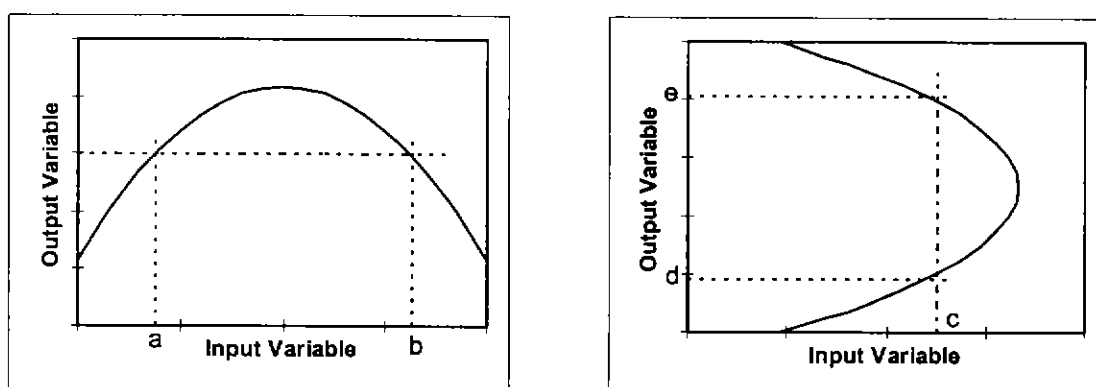


Figure 8.1 - Input Multiplicity (left) and Output Multiplicity (right)

### 8.1.2 Examples of Input Multiplicity

The effects of various operating variables on two hybrid reactive distillation columns were described in Chapter 4, Section 4.1. The reboiler duty (Section 4.1.7) was shown to have a bidirectional effect on the principal performance parameters (i.e. the ether purity and the isobutene conversion): depending on the magnitude of the reboiler duty, an increase in the duty could either increase or decrease the purity or the conversion, as indicated in Figure 4.3 which was constructed using simulation results for the 10 stage ETBE column. Input multiplicity exists in this case since some output conditions (e.g. the bottoms temperature,  $T_b$ ) map to more than one value of a specific input variable (e.g. the reboiler duty,  $Q_R$ ) while all other input conditions are the same, as shown in Table 8.1.

**Table 8.1 - Input Multiplicity in an ETBE Column**

	<b>Steady State A</b>	<b>Steady State B</b>
<i>Output Condition</i>		
Bottoms temperature (°C )	150	150
<i>Input Conditions</i>		
Hydrocarbon feed composition	40% isobutene, 60% n-butene	40% isobutene, 60% n-butene
Methanol excess (mol%)	5%	5%
Total feed rate (L/min)	0.76	0.76
Pressure (kPa-g)	950	950
Reflux rate (L/min)	2.50	2.50
Reboiler duty (kW)	<b>8.20</b>	<b>8.97</b>

A similar, bidirectional dependence of the column performance on the reboiler duty is seen with the MTBE system. Table 8.2 describes the configuration of a 17 stage MTBE column (Nijhuis et al., 1993). Figure 8.2 shows the bidirectional effect of the reflux rate (L) on the bottoms temperature of this column for a constant bottoms yield of 35.0% by volume. Input multiplicity is present since, for example, a bottoms temperature of 145°C results with reflux rates of 130 and 535 m<sup>3</sup>/hr.

**Table 8.2 - MTBE Column Characteristics**

<b>Design Parameter</b>	<b>Value</b>
Rectifying stages (including total condenser)	3
Reactive stages	8
Stripping stages (including partial reboiler)	6
Feed stage	lowest reactive stage
Hydrocarbon feed composition (mol %)	36% isobutene, 64% n-butane
Stoichiometric methanol excess (mol %)	10 %
Total feed rate	2752 kmol/hr
Overhead pressure	1000 kPa-g
Reflux ratio	~7.0

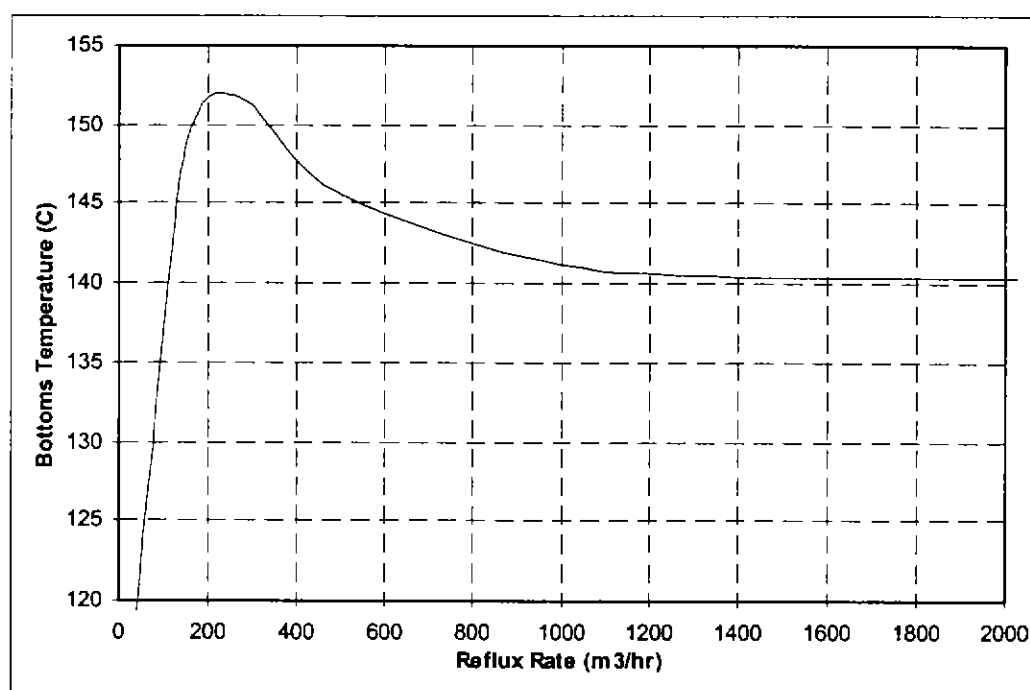


Figure 8.2 - Input Multiplicity in a MTBE Reactive Distillation Column

The two examples of input multiplicity indicated above can also be described analytically. The ETBE column multiplicity satisfies the condition given by equation (8.1) while the MTBE column multiplicity satisfies equation (8.2). A more general expression of this condition is given by equation (8.3), which describes any stationary point between an input variable ( $x_1$ ) and an output input variable ( $y$ ) with other inputs ( $x_2$ ) constant.

$$\left( \frac{\partial T_b}{\partial Q_R} \right)_L = 0 \quad (8.1)$$

$$\left( \frac{\partial T_b}{\partial L} \right)_{Q_R} = 0 \quad (8.2)$$

$$\left( \frac{\partial y}{\partial x_1} \right)_{x_2} = 0 \quad (8.3)$$

### 8.1.3 Causes of Input Multiplicity

#### 8.1.3.1 Fundamental Explanation

The non-reactive distillation residue curve diagrams in Chapter 5 (Section 5.1.1) show that the ETBE and the MTBE system each comprise two distillation regions separated by a distillation boundary. The phase behaviour of each system is governed by the low boiling azeotrope, ETBE-ethanol or MTBE-methanol, and the distillation boundary extends from this azeotrope to the unstable node in each system (i.e. pure  $C_4$  or the low boiling azeotrope

between  $C_4$  and methanol). The distillation boundary cannot be crossed unless the components react so that, in non-reactive distillation, the distillation products are constrained to the same distillation region as the feed.

Homogenous reactive distillation is subject to a similar set of constraints due to the reactive phase behaviour: reactive azeotropes create reactive distillation boundaries that cannot be crossed. It should be noted that the reactive residue curve diagrams for the ETBE and the MTBE system (Section 5.1.2) indicate that no such azeotropes exist so that there is only one reactive distillation region in each case. In both non-reactive distillation and homogenous reactive distillation, the trajectories of the residue curves are readily predicted and extend from the most volatile node to the least volatile node in the distillation region that contains the feed. This occurs if there are one, two or more distillation regions. In all cases, the temperature of the residue increases steadily along the trajectory from the unstable node to the stable node.

These considerations, although based on a batch distillation process, carry over to continuous distillation and approximately reflect the product compositions obtained by varying the bottoms yield from 100% to 0% of the feed. The residue curve diagrams predict a steady decrease in the concentration of the least volatile component and a steady increase in the temperature of the bottoms product.

Hybrid reactive distillation is unusual since the distillation boundary that exists for the non-reactive sections of the column can be traversed via the reaction which occurs in the reactive section of the column. The feasible product region is effectively unconstrained. The stable node that directs the residue trajectory can change from one distillation region to the other as the bottoms yield decreases, depending on the extent of the reaction and the path of the reactive section of the hybrid residue trajectory. Consequently, it is possible for the bottoms composition to change such that the temperature decreases rather than increases.

The reactive residue curves for the ETBE and the MTBE system terminate at the ethanol and the methanol node, respectively. This controls the direction of the hybrid residue trajectories such that the first drop of bottoms is always pure ethanol or methanol. Since the ether product is less volatile than the reactants and the ETBE and MTBE nodes are feasible product compositions due to the influence of the reaction, the maximum bottoms temperature exceeds the bottoms temperature at the stable node (i.e. the first drop of bottoms product). Note that this only occurs in a hybrid distillation system. The presence of a global maximum temperature (i.e. near the ETBE or MTBE node) higher than the local

maximum (i.e. at the ethanol or methanol node) produces the possibility of bidirectionality, where the bottoms temperature can decrease as the distillate yield is increased. This is the basis for input multiplicity in this system.

#### *8.1.3.2 Mechanistic Explanation*

Input multiplicity in hybrid reactive distillation can also be explained from a mechanistic perspective by considering the conditions required for high ether purity in the bottoms product. Reactive distillation is only feasible if the temperature and pressure required for the reaction and the separation coincide. If the conditions required for effective fractionation are such that temperatures are too high for effective reaction (e.g. the reaction is restricted by thermodynamics) or too low (e.g. the reaction is restricted by kinetics or the availability of reactants), reactive distillation cannot be utilised successfully. This premise implies that the column operating conditions must be optimised to concurrently achieve adequate reaction and separation and, therefore, the existence of a maximum ether production rate. Since the purity will decrease on either side of the optimum, there will always exist two input conditions for at least some values of any output conditions other than at the stationary point. This exactly describes the conditions for input multiplicity.

The important parameters for optimisation are the column pressure and the heat input (i.e. the reboiler duty) since these directly affect the stage-to-stage temperatures within the column. The effects of these parameters were discussed extensively in Chapter 4 and bidirectionality with respect to the reaction rate and the bottoms composition was demonstrated and explained for both the pressure and the reboiler duty. Essentially, two operating regions exist for the hybrid column: separation controlled (heat input below the optimum) and reaction controlled (heat input above the optimum). A given value of any output condition can usually be found for input conditions in both regions. For example, a reboiler temperature of 130°C can be produced with a low and a high reboiler duty (i.e. there is input multiplicity).

Typically, a low heat input will produce operating conditions which are favourable for the reaction (i.e. high conversion of reactants) but provide insufficient vapour-liquid traffic for good separation (i.e. low ether purities). The converse applies for a high heat input. A narrow range of heat inputs (or bottoms yields, etc.) will permit a high conversion and a high purity to be obtained simultaneously.

## 8.2 OUTPUT MULTIPLICITY

### 8.2.1 Output Multiplicity due to Unit Singularities

Jacobsen and Skogestad (1991) presented an example of an ideal distillation process that yields multiple steady states (i.e. it exhibits output multiplicity) when mass units were used but only one steady state when molar units were used. They argued that the change of units created the multiplicity as the partial derivative of the mass flow with respect to the molar flow was not necessarily always positive. They proposed the term *input transformation* to describe this behaviour. Later, Güttinger and Morari (1997) considered singularities in the mass-molar relationships with respect to output multiplicity in reactive distillation and proposed a geometrical technique to analyse singularities which occur with external specifications (i.e. product flow rates). However, they were unable to provide an example of a reactive distillation system where multiplicity was directly attributable to a singularity.

A more general designation of this condition is proposed here: *unit singularities*, referring to any stationary point in an otherwise smooth relationship between input variables. This description is preferred to others since it may pertain to a singularity in dissimilar variables (e.g. the relationship between the molar boilup and the reboiler duty). This is important since these singularities are equally capable of causing multiplicity. A specific example of a singularity in the mass-molar relationship causing an output multiplicity in a reactive distillation column is also provided.

The column considered was a 30 stage ETBE reactive column with the configuration given by Table 8.3. The output multiplicity is shown in Figure 8.3, which is part of a bifurcation diagram for this system (i.e. the locus of steady state solutions for a set of inputs that differs by one parameter only - the independent variable) for the conditions given in Table 8.3. This data was obtained from a series of Pro/II simulations. There are three separate steady state solutions for all bottoms yields between 35.2% and 36.6% of the feed rate. The salient features of the upper and lower branches are indicated in Table 8.4, which pertains to points A and B on Figure 8.3.



Table 8.3 - 30 Stage ETBE Column Characteristics

Design Parameter	Value
Rectifying stages (including total condenser)	8
Reactive stages	7
Stripping stages (including partial reboiler)	15
Feed stage	uppermost stripping stage
Hydrocarbon feed composition (mol %)	25% isobutene, 75% n-butenes
Stoichiometric ethanol excess (mol %)	0 %
Total feed rate (kmol/hr)	100 kg/hr
Overhead pressure	700 kPa-g
Reflux rate	81.3 kg/hr

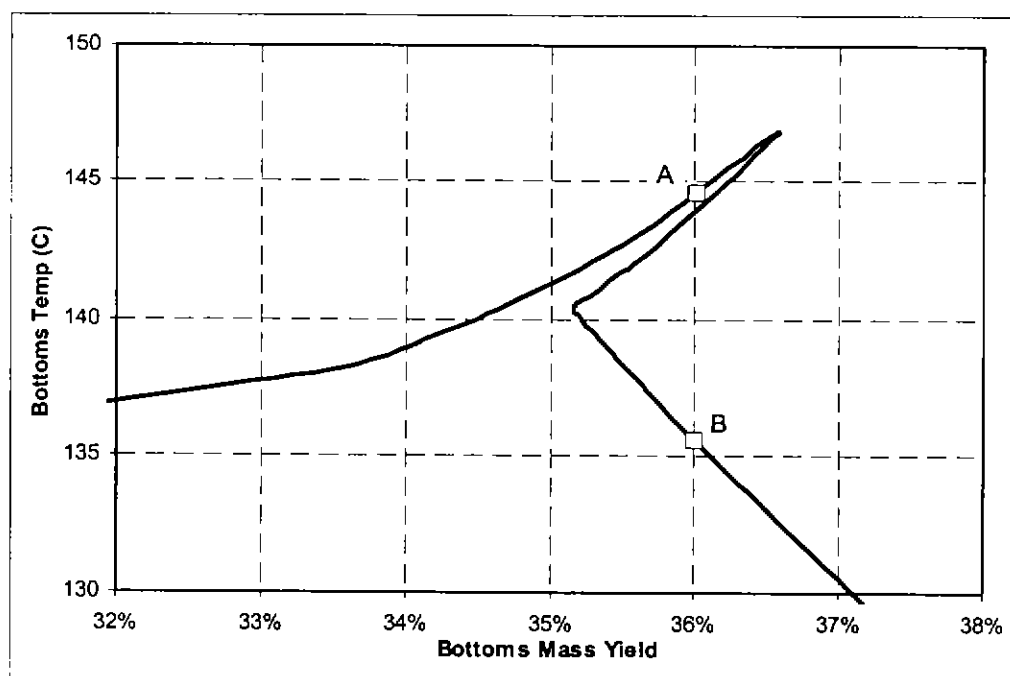


Figure 8.3 - Output Multiplicity due to a Unit Singularity in a Reactive ETBE Column

Table 8.4 - High and Low Conversion Steady States for ETBE Column

Property	High Conversion Steady State Value (Point A)	Low Conversion Steady State Value (Point B)
Overall isobutene conversion (mol %)	90.7	84.1
Bottoms ETBE purity (mol %)	90.4	79.6
Reboiler temperature (°C)	144.7	135.7
Reboiler duty	0.914	0.920
Boilup ratio (molar basis)	4.67	4.33
Bottoms yield (molar basis w.r.t. feed)	20.1%	21.1%
Reflux ratio	1.272	1.271

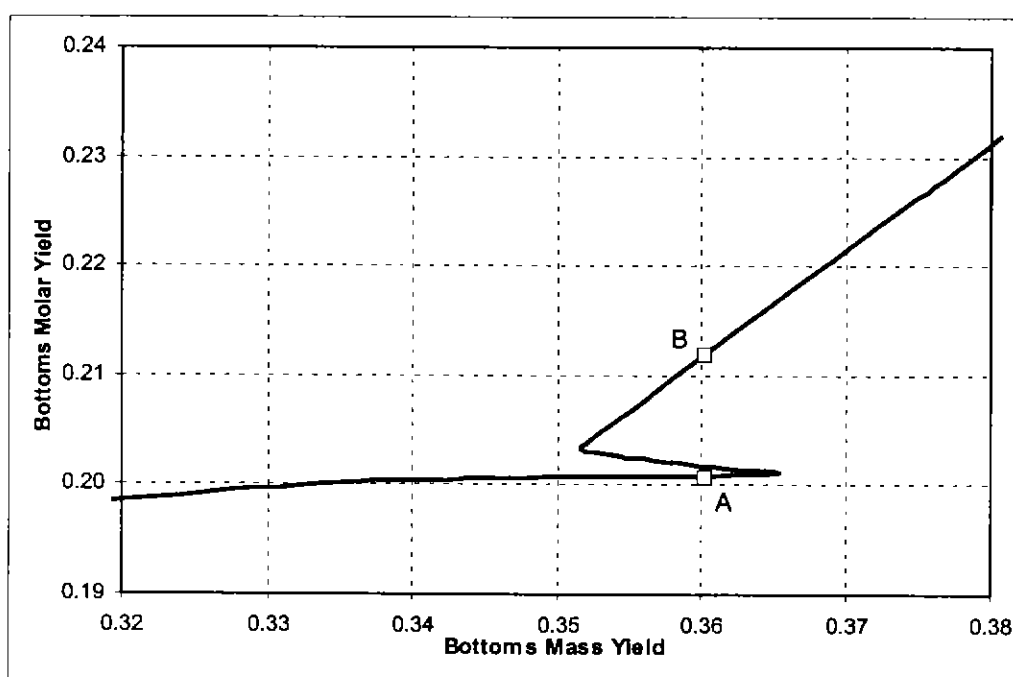


Figure 8.4 - Singularities in the Bottoms Mass-Molar Relationship

The cause of the output multiplicity in this column is a singularity in the relationship between the molar bottoms flow ( $B$ ) and the mass bottoms flow ( $B_m$ ), as shown in Figure 8.4. The stationary points from this plot satisfy condition (8.4), which is sufficient for multiplicity. Equation (8.5) implies a unit singularity between the molar boilup rate ( $V$ ) and the reboiler duty ( $Q_R$ ) and, although not present in this column, such a singularity is also sufficient for output multiplicity. Indeed, any singularity between a molar input (i.e. molar reflux, boilup, distillate and bottoms rates) and the actual input (i.e. volumetric or mass reflux, distillate and bottoms rates, and the reboiler duty) will cause an output multiplicity.

$$\left( \frac{\partial B_m}{\partial B} \right)_L = 0 \quad (8.4)$$

$$\left( \frac{\partial Q_R}{\partial V} \right)_L = 0 \quad (8.5)$$

### 8.2.2 Output Multiplicity due to the Influence of the Energy Balance

This cause of multiplicity was also originally described by Jacobsen and Skogestad (1991) with respect to an ideal, binary, non-reactive distillation column. In certain cases, multiple steady states were not observed when the energy balances around each distillation stage were neglected (i.e. the constant molar overflow, CMO, solution was considered). Although they only considered non-reactive distillation, this concept is equally valid in other areas, including reactive distillation and hybrid columns.

Essentially, multiple steady states arise where the energy balances produce a change in the product compositions that has an opposite and more substantial effect on the product flows than the direct effect of the change in the internal liquid (or vapour) flow. This is summarised by inequalities (8.6) and (8.7) which are necessary and sufficient conditions for multiple steady states (Jacobsen and Skogestad, 1991). Under these conditions, an increase in the reflux rate has an inverse effect on the bottoms product draw rate or, similarly, an increase in the boilup rate decreases the distillate draw rate. Thus, multiple values of the product rate (and, therefore, product composition) can exist for a single value of the reflux or boilup rate.

$$\left( \frac{\partial(B+V)}{\partial L} \right)_V < 0 \quad (8.6)$$

$$\left( \frac{\partial(D+L)}{\partial V} \right)_L < 0 \quad (8.7)$$

The heat of reaction has been postulated as a possible cause for multiple steady states in reactive distillation (Jacobs and Krishna, 1993). In light of the above explanation of the effect of the energy balances in the distillation model (or, conversely, the effect of ignoring the energy balances), the basis for the postulation becomes clearer: the heat of reaction introduces another term to the energy balances which will create a difference between the molar flow rate entering and leaving a stage. This effect may be directionally different from the *normal* effect of the internal flow rate. For example, increasing the reflux rate may have

a beneficial effect on the net reaction rate that might result in an effective decrease in the liquid leaving a reactive stage. If this effect is substantial enough, it will result in a change of sign of  $\left(\frac{\partial B}{\partial L}\right)_v$  and, therefore, satisfy condition (8.6) and result in an output multiplicity.

Figure 8.5 shows a section of the bifurcation diagram for constant reflux rate in the 17 stage MTBE column described in Table 8.2. Multiple steady states exist for boilup rates of 80-82 kmol/hr if the simulation model includes the energy balance for each theoretical stage but only one steady state if the results are obtained with a CMO model. The offset between the two curves is also a result of the exclusion of energy balances as the heat of reaction is not considered in the CMO case. The cause of the observed multiplicity can be seen in Figure 8.6 which shows the influence of the energy balance on the relationship between the boilup rate and the distillate rate for the same section of the bifurcation diagram. Condition (8.7) is satisfied at boilup rates of 80-82 kmol/hr with the energy balance model while  $\left(\frac{\partial D}{\partial V}\right)_L$  is always greater than zero with the CMO model.

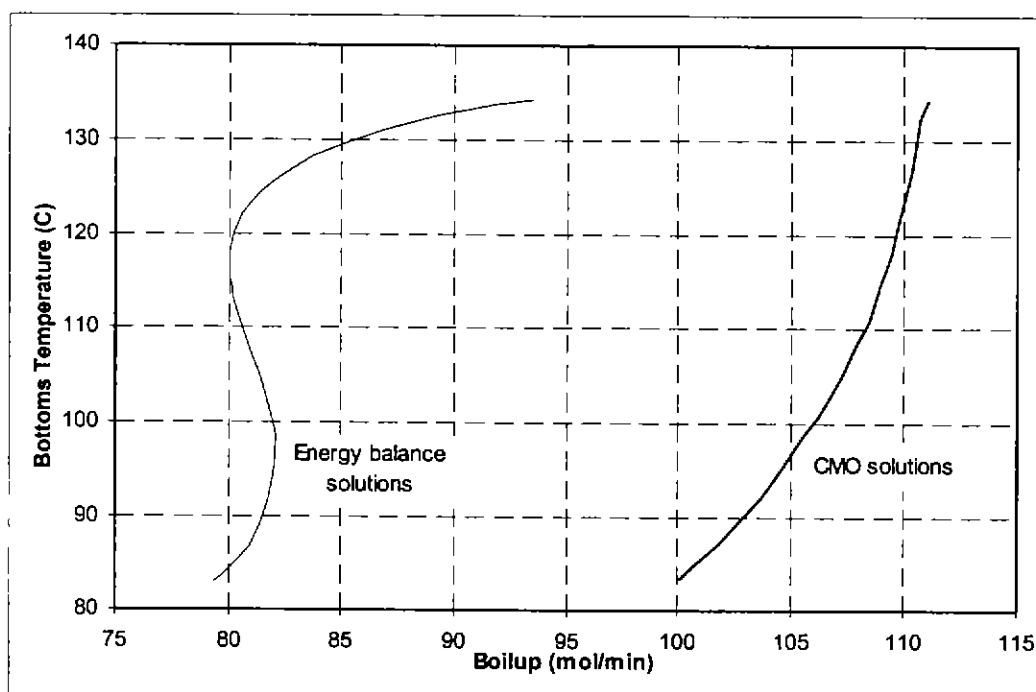
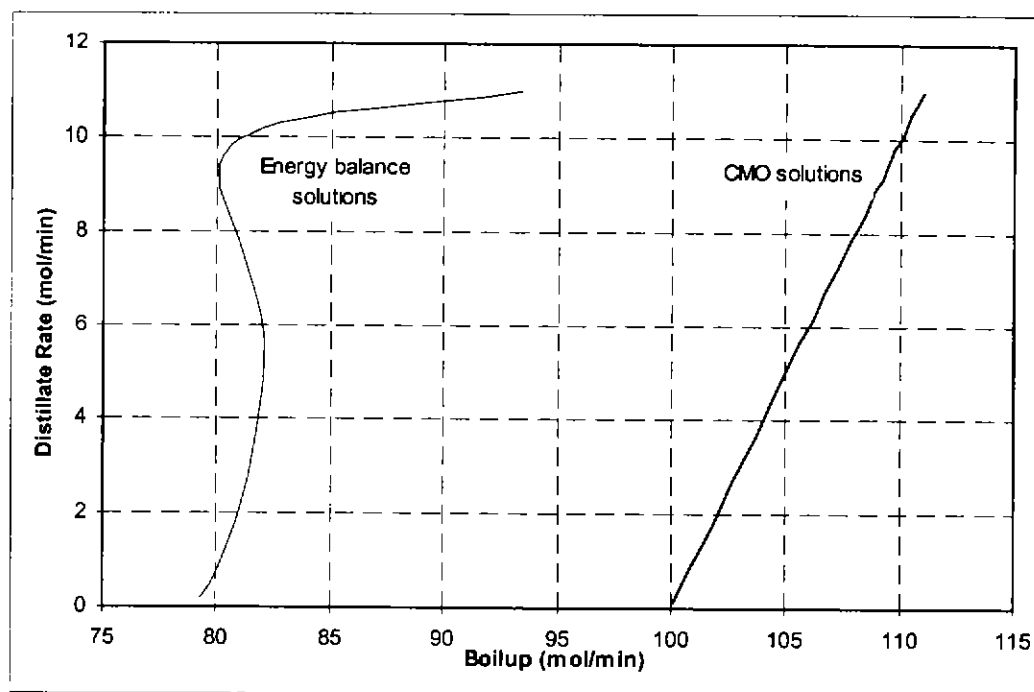


Figure 8.5 - Multiple Steady States Caused by the Energy Balance



**Figure 8.6 - Effect of Molar Boilup on the Distillate Product Rate**

### 8.2.3 Output Multiplicity due to Azeotropes

Azeotropes in mixtures of three or more components can result in a completely different type of distillation multiplicity. In this case, the multiplicity will be observable in any type of unit (i.e. molar, volumetric, mass, duty, etc.) and can be detected with a rigorous model or with a CMO model. Bekiaris and Morari (1993) were the first to elucidate the link between azeotropes and multiplicity in non-reactive distillation and were able to develop a geometrical tool to detect multiplicities without a bifurcation diagram. The tool,  $\infty/\infty$  analysis, allows the product composition to be predicted from the feed composition and a product rate specification, assuming the column fractionation is sufficiently close to the ideal case (i.e. infinite stages and infinite reflux ratio, hence  $\infty/\infty$ ).

The  $\infty/\infty$  approach is an excellent tool but it still has several shortcomings: the fractionation characteristics (i.e. the number of stages, etc.) required for the predictions to be accurate is uncertain so that the analysis is not always applicable for finite columns; to be applied, the system must be representable as a pseudo-ternary mixture; only single-feed, dual-product columns can be analysed; and, no predictions can be made for internal specifications (e.g. the reflux rate or ratio, or the reboiler duty). However,  $\infty/\infty$  analysis can be applied to reactive columns if transformed composition co-ordinates are used (Güttinger and Morari, 1997). The transformations required are the same as those proposed by Ung and Doherty (1995) and others, and were described in Chapter 5 (Section 5.1.3).

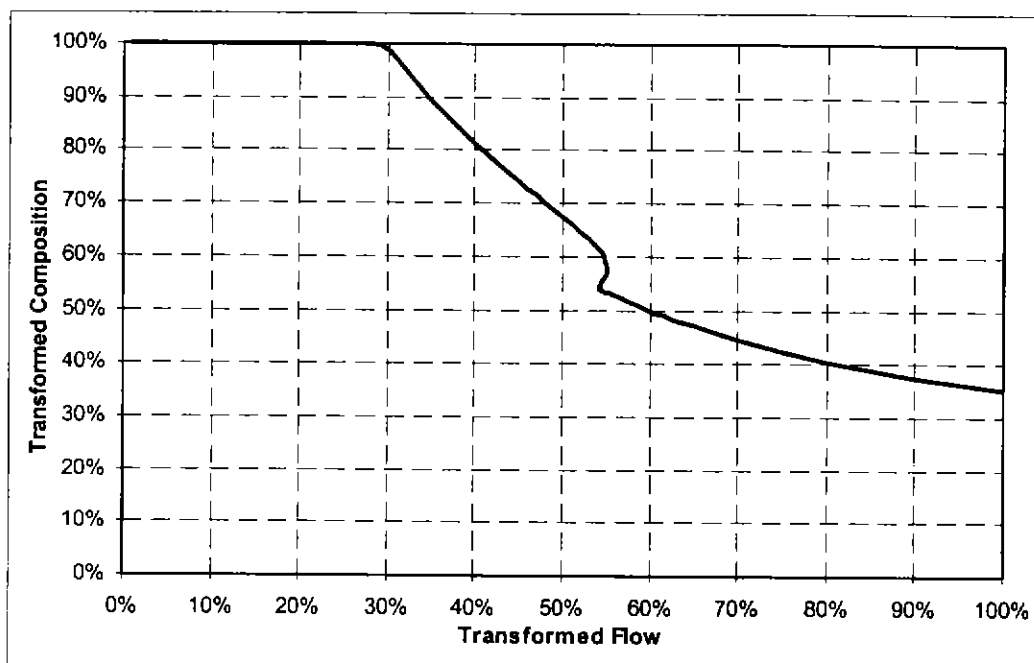
The principal result which is obtained from  $\infty/\infty$  analysis is the region in composition space which will produce multiple steady states. The analysis is independent of the column configuration and only requires basic VLE data on the components and the azeotropes. Thus, an analysis that has been completed for the MTBE system is adequate for all MTBE columns. Such an analysis has been completed previously (Güttinger and Morari, 1997) and suggests that a feed which consists of 25% isobutene, 35% methanol and 40% n-butenes (40% stoichiometric excess of methanol) will produce multiple steady states. According to the  $\infty/\infty$  technique, this type of multiplicity can be detected more easily in the transformed composition co-ordinates.

The effectiveness of the  $\infty/\infty$  analysis was evaluated here for two different hybrid MTBE columns. Figure 8.7 was constructed using a bifurcation analysis of the column configuration indicated in Table 8.2 with the given feed composition and a constant reflux to feed ratio of 3.5. Figure 8.8 considers the same combination of feed composition and reflux ratio in a 10 stage column with two rectifying stages (including a total condenser), one reactive stage and seven stripping stages (including a partial reboiler). The feed to this column is split between the stage immediately above the reactive stage and the stage uppermost stripping stage. The transformed flow and composition are defined as follows:

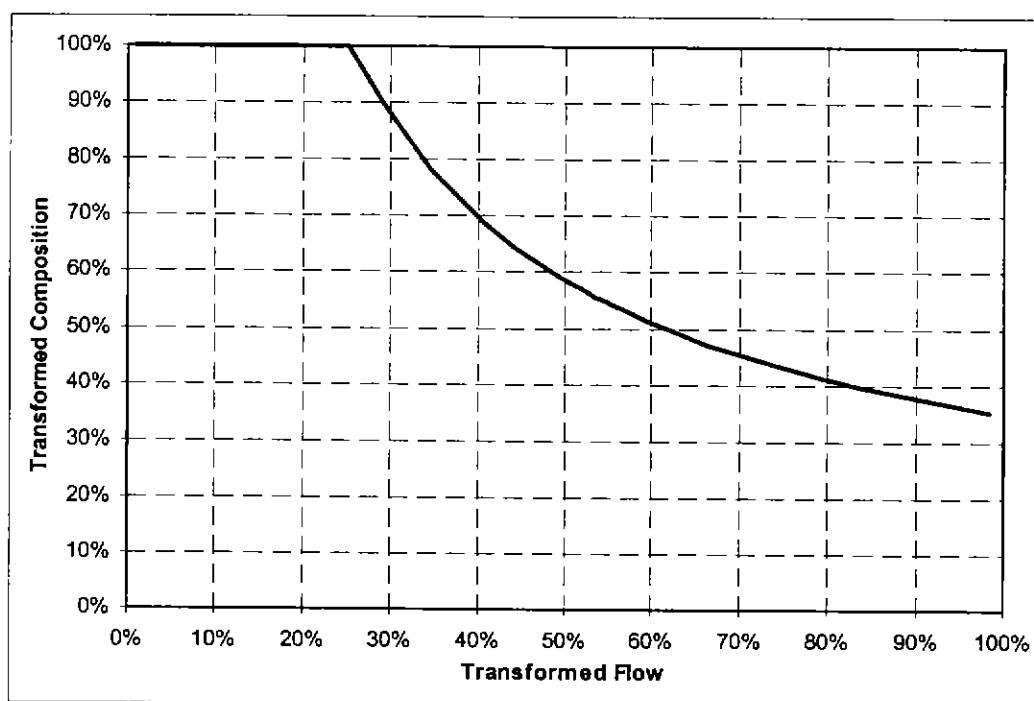
$$X = \frac{x_{MeOH} + x_{MTBE}}{1 + x_{MTBE}} \quad (8.8)$$

$$B' = \frac{B}{1 + x_{MTBE}} \quad (8.9)$$

The  $\infty/\infty$  analysis correctly predicts the multiplicity in the 17 stage column but does not recognise that the multiplicity disappears in a shorter column. The analysis of the 10 stage column is a stringent test for the  $\infty/\infty$  technique as there are several factors which contradict the  $\infty/\infty$  assumptions: the column contains both reactive and non-reactive sections; there are two feed points; and the column is relatively short (only 10 stages). It is, therefore, not surprising that the  $\infty/\infty$  predictions are incorrect in this case.



**Figure 8.7 - Bifurcation Results for a 17 Stage MTBE Reactive Distillation Column with a Feed Composition Predicted to Produce Multiple Steady States by an  $\infty/\infty$  Analysis**



**Figure 8.8 - Bifurcation Results for a 10 Stage MTBE Reactive Distillation Column with a Feed Composition Predicted to Produce Multiple Steady States by an  $\infty/\infty$  Analysis**

Since there is uncertainty regarding the predictions for finite columns, perhaps the best application of the  $\infty/\infty$  technique is for screening reactive distillation systems and feed compositions for the possible existence of multiple steady states. For example, the reactive

residue curve diagram for ETBE, in transformed variables, shows no azeotropes. Although an azeotrope exists between ETBE and ethanol, it is not independent of the reaction. Therefore, *azeotropic* multiple steady states will not be present in ETBE reactive distillation for any feed composition in any column configuration. However, this does not preclude the possibility of another type of multiplicity occurring!

#### 8.2.4 Output Multiplicity due to Reaction Hysteresis

A fourth multiplicity mechanism, reaction hysteresis, is proposed here to explain that multiple steady states observed in simulations of the hybrid MTBE column described by Table 8.2. The multiplicity in this column denoted by D-E in Figure 8.9 cannot be adequately explained by any of the causes discussed in Sections 8.2.1-8.2.3.

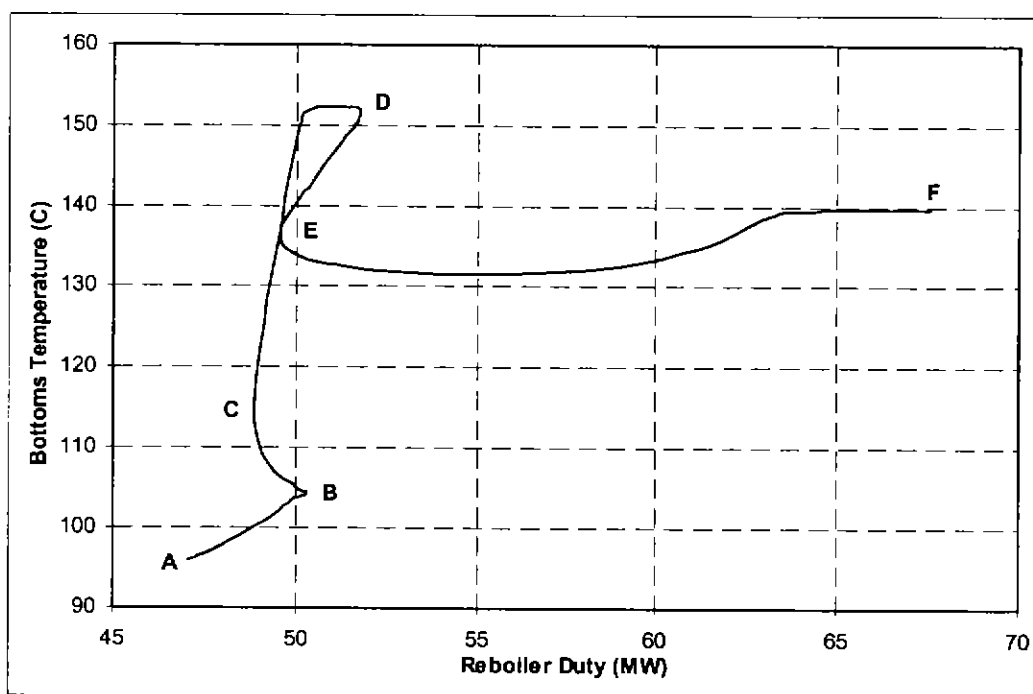


Figure 8.9 - Output Multiplicities in a Hybrid MTBE Column

This multiplicity is not caused by singularities in any mass-molar relationships as the multiplicity persists if molar units are considered. Neither is the multiplicity caused by energy balance effects since the multiplicity also persists if the energy balance is ignored. It is unclear whether azeotropes could be responsible for this multiplicity since the mechanism has only been explained for material-balance specifications (e.g. constant distillate or bottoms product rate) and an energy-balance specification was used in this case (i.e. constant reflux rate). However, the feed composition is outside the region which produces multiple steady states (as determined via an  $\infty/\infty$  analysis) so that an explanation based on the VLE characteristics only appears tenuous. Güttinger and Morari (1997) suggested that



interactions between the reactive and non-reactive column sections might extend the boundaries of the multiplicity feed region but there appears to be little evidence for this speculation and the implications for energy-balance specifications (e.g. constant reboiler duty or reflux rate, as in this case) are unclear. Thus, an alternative explanation for the unusual behaviour of this column is required.

It is proposed that, in this case, the multiple steady states arise from interactions between the reactive and non-reactive column sections via the effect that the non-reactive sections have on the reaction zone conditions. This type of multiplicity is applicable to any hybrid column with any type of specifications, and is caused by a change in the reaction zone condition that is propagated and reinforced by the fractionation changes that concurrently resulted from the original disturbance. A very high process gain is possible from this combination of effects but, more importantly, the two effects may not reinforce each other in the opposite direction. This pattern describes a process hysteresis, which is a sufficient condition for multiplicity.

To understand the proposed mechanism, it is important to consider necessary and sufficient conditions for output multiplicity. Previous authors (e.g. Hauan et al., 1995; 1997) have discussed multiplicity in relation to strongly non-linear behaviour but non-linearity is only necessary and not sufficient for output multiplicity. Provided that a change in an operating condition is reversible, the bifurcation diagram for that parameter will be smooth and only one steady state will exist. A distinctive 'S' shape is seen in the bifurcation diagram where there are multiple steady states. The 'S' shape effectively defines a process hysteresis (i.e. a non-reversible change in operating conditions) which is both a necessary and sufficient condition for output multiplicity. One bifurcation branch is accessible only by increasing the bifurcation parameter while the other branch is accessible only by decreasing the bifurcation parameter.

The application of reaction hysteresis to this hybrid MTBE column is as follows. Where the reactive section of the column is cool and lean in methanol, increasing the boilup rate strips methanol from the bottoms product and promotes the MTBE synthesis reaction on the reactive stages. This is facilitated by the minimum-boiling azeotropes that form between methanol (the heaviest reactant) and the various C<sub>4</sub> components. However, an increase in the boilup rate causes the phase equilibrium temperature to rise that tends to suppress the synthesis reaction due to its exothermic nature.

The duality of effects continues in this way with increasing boilup until a critical point is reached when the effect of the increasing temperature predominates and the decomposition reaction is favoured. This produces more methanol which propagates the trend of rising temperatures (the reactive residue curve terminates at methanol and not MTBE) and escalates the MTBE decomposition rate. The column profile then goes through a catastrophic change before stabilising to a new operating point with higher concentration of methanol in the reaction zone (and upper stripping section) and a lower overall conversion of reactants to MTBE. In reverse, a decrease in the boilup rate has only a slight effect on the temperature and composition profiles as the two effects no longer reinforce each other. The situation is somewhat analogous to a reaction runaway although fractionation effects trigger the runaway rather than kinetic effects.

As with multiplicities due to the presence of azeotropes in the VLE, the column configuration (i.e. the number of theoretical stages, and the internal vapour and liquid flow rates) can affect the presence of a reaction hysteresis. With fewer stages and lower internal flows (i.e. low reflux and boilup ratios), composition differences between adjoining stages are lessened, and there is less scope for changes in the stage-to-stage temperatures and compositions to propagate and multiply.

Reaction hysteresis, as described above, is dependent on interactions between the reactive and non-reactive column sections, and is independent of reaction kinetics, the column energy balance and singularities in the mass-molar relationships. This type of behaviour exactly fits the simulation observations and could be responsible for the output multiplicity shown in Figure 8.9.

#### **8.2.5 Parallels Between the Energy Balance and the Unit Singularities Causes**

The explanations for multiplicity caused by unit singularities and by energy balance effects are fundamentally different but there are similarities between the two mechanisms which suggest that a unified method of analysis might be available. In fact, equations (8.4) and (8.5) (the conditions for multiplicity due to unit singularities) can be combined with inequalities (8.6) and (8.7) (the conditions for multiplicity due to the influence of the energy balance) according to equations (8.10) and (8.11). These equations yield new, more general conditions for multiplicity (inequalities 8.12 and 8.13) and do not include any molar flow terms.

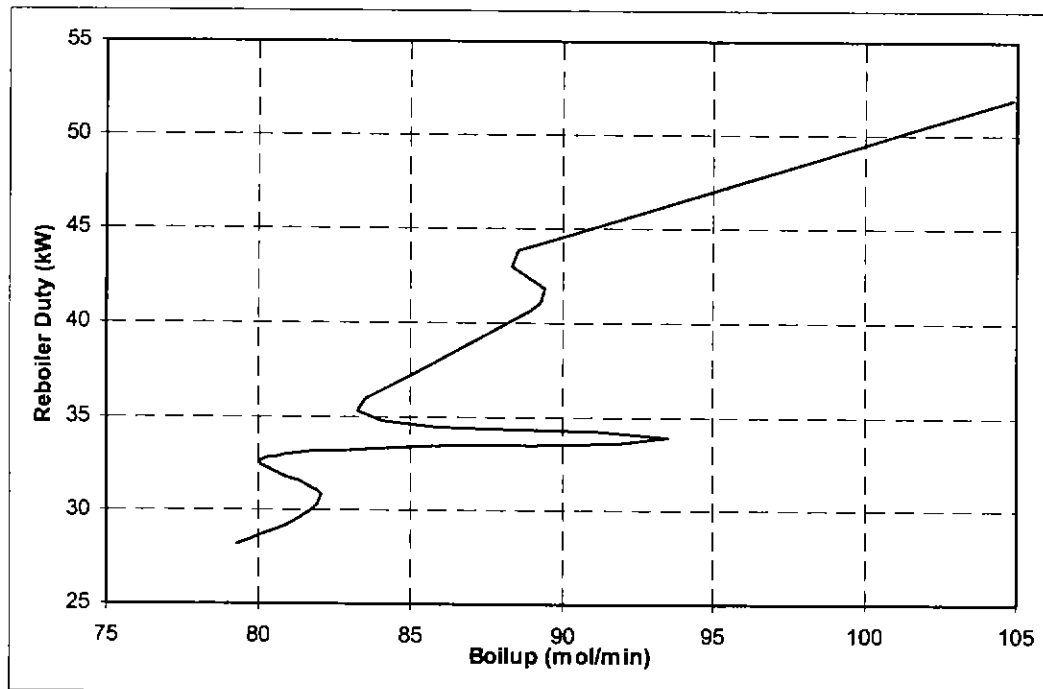
$$\left(\frac{\partial B_m}{\partial L_m}\right) = \left(\frac{\partial B}{\partial L}\right) \times \left(\frac{\partial B_m}{\partial B}\right) \times \left(\frac{\partial L_m}{\partial L}\right)^{-1} \quad (8.10)$$

$$\left(\frac{\partial D_m}{\partial Q_R}\right) = \left(\frac{\partial D}{\partial V}\right) \times \left(\frac{\partial D_m}{\partial D}\right) \times \left(\frac{\partial Q_R}{\partial V}\right)^{-1} \quad (8.11)$$

$$\left(\frac{\partial B_m}{\partial L_m}\right) < 0 \quad (8.12)$$

$$\left(\frac{\partial D_m}{\partial Q_R}\right) < 0 \quad (8.13)$$

Any of the partial derivatives on the right hand sides of equations (8.10) and (8.11) can be negative and, thereby, cause multiplicity. If two of the derivatives are negative at the same time, the effects will cancel each other and the multiplicity will only be observed for molar units. An example of this is provided by the MTBE column described in Table 8.2. Figure 8.6 shows  $\left(\frac{\partial D}{\partial V}\right) < 0$  and Figure 8.10 shows  $\left(\frac{\partial Q_R}{\partial V}\right) < 0$ . The two curves have the same shape so that  $\left(\frac{\partial D_m}{\partial Q_R}\right) > 0$  for all values of the boilup rate.



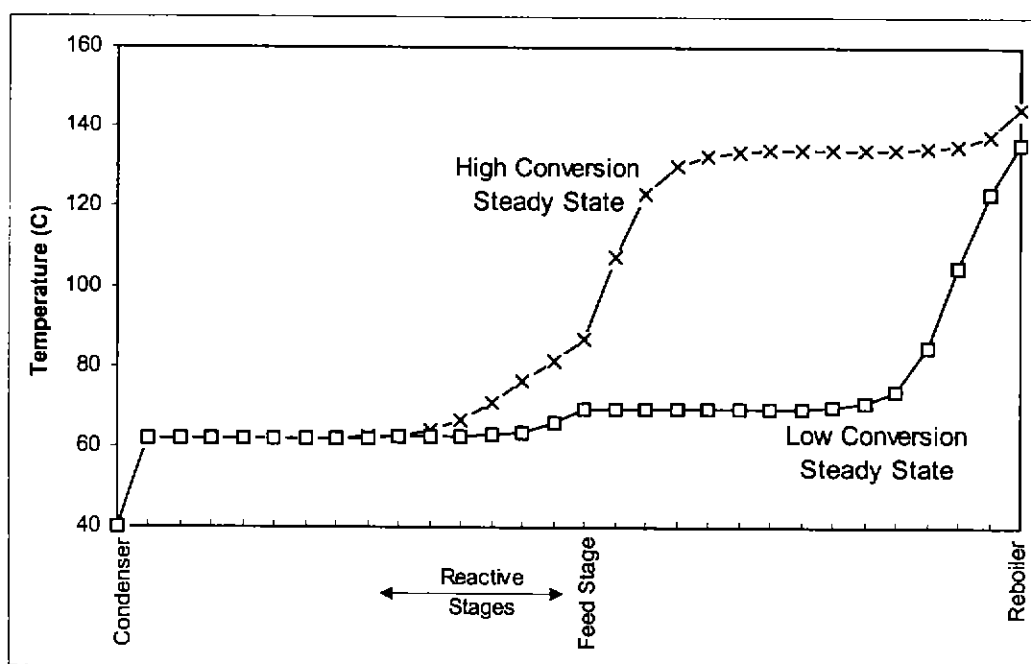
**Figure 8.10 - Singularities Between the Reboiler Duty and the Molar Boilup**

Unfortunately, conditions (8.12) and (8.13) can only realistically be evaluated using a bifurcation analysis with a rigorous simulation model of the system under study. This restricts the application of these equations but other tools (especially those that rely on molar inputs) are not guaranteed to be accurate in all cases.

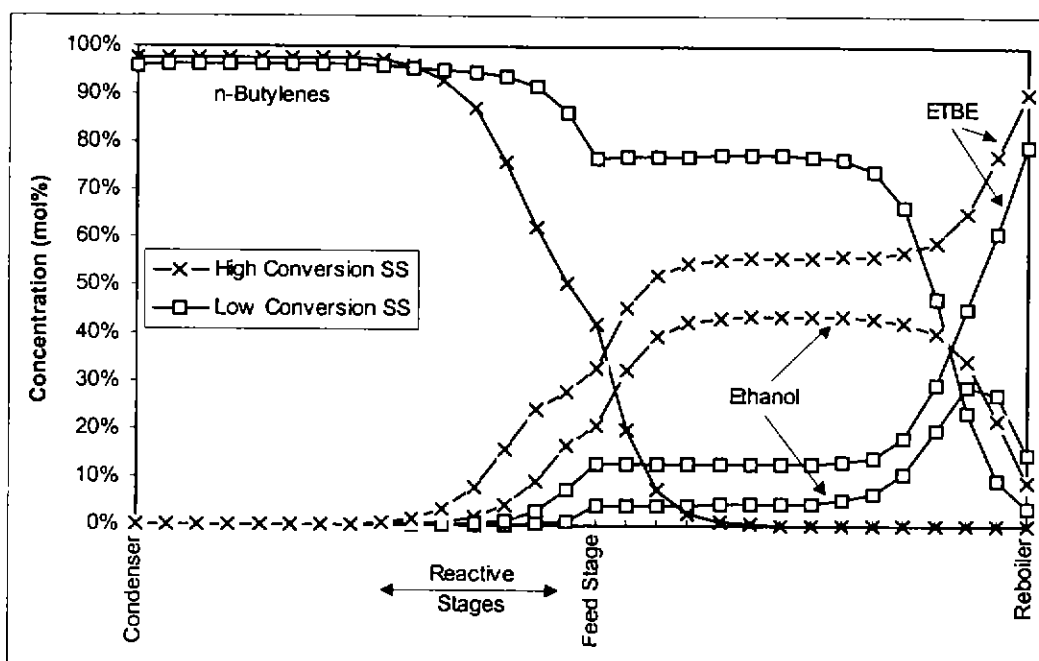
### 8.2.6 Mechanistic Interpretation

The multiplicity shown in the ETBE column due to unit singularities (Figure 8.3) was investigated further in order to interpret the differences between the parallel steady states from a mechanistic perspective. It was considered that an understanding of the changes and differences would have practical importance. Other multiplicities could be investigated similarly although the mechanism might be quite specific.

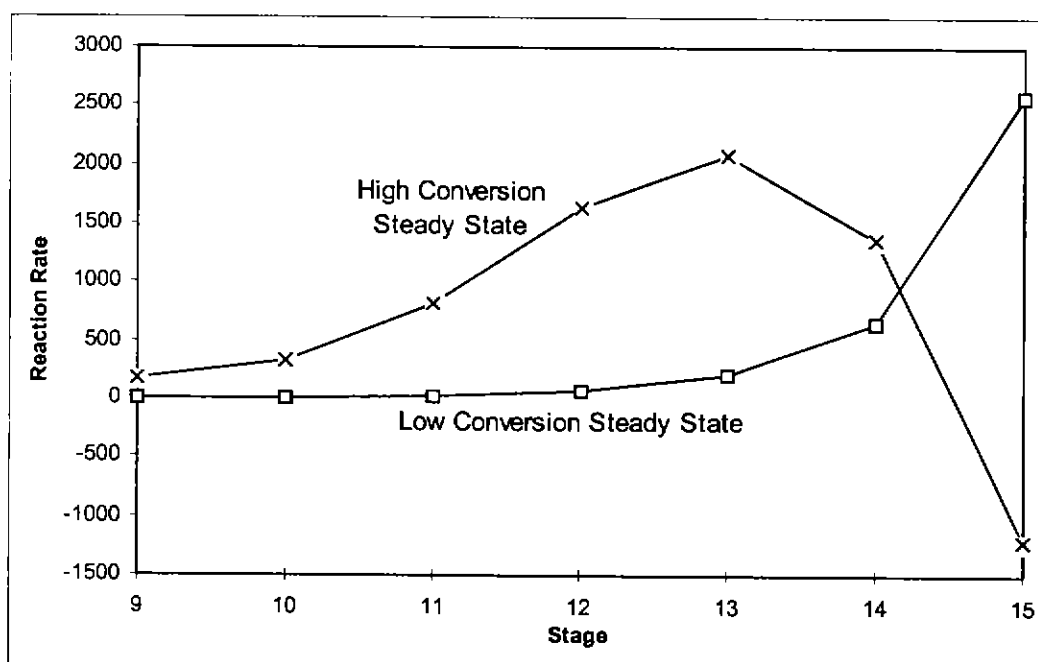
A comparison between the two steady states described in Table 8.4 is provided by Figures 8.11-8.13 which compare the temperature profiles (Figure 8.11), the composition profiles (Figure 8.12) and the reaction rate profiles (Figure 8.13) for points A and B. The most striking contrasts are the stripping section temperatures; (b) the stage-to-stage compositions in the stripping section; and (c) the reaction rate on the lowermost reactive stage.



**Figure 8.11 - Temperature Profiles in the ETBE Column**



**Figure 8.12 - Selected Composition Profiles in the ETBE Column**



**Figure 8.13 - Reaction Rate Profiles in the ETBE Column**

Figures 8.11 and 8.12 indicate that the rectifying section of the column is similar in both the high and the low conversion steady states. However, slight changes in the stage-to-stage compositions are magnified by the different reaction rate profiles (Figure 8.13) so that there are substantial differences in the temperature and compositions on the lower reactive stages. The effect of fractionation in the reaction zone is to concentrate ethanol (if present) near the lower reactive stages. This promotes the synthesis reaction due to the increased reactant

availability but eventually initiates decomposition if the elevated phase temperature (caused by the increasing ethanol concentration and the formation of ETBE) reduces the reaction equilibrium constant too much. If there is no ethanol present in the reaction zone, the synthesis reaction is suppressed even though the reaction equilibrium constant is higher.

Thus, the crucial consideration is the supply of ethanol to the reaction zone. This is dependent on the fractionation in the stripping section and the stage-to-stage compositions in the stripping section. It is proposed that a high concentration of n-butylenes induces a pseudo-binary separation between  $C_4$ s and ethanol/ETBE, while a low concentration of n-butylenes allows a pseudo-binary separation of ethanol (and all lighter components) and ETBE. It is important to realise that ETBE is the heavy boiler in this system even though the boiling point of ethanol is higher than the boiling point of ETBE as the vapour pressure curves of ethanol and ETBE intersect at around 300 kPa. Although the azeotrope between ethanol and ETBE creates a distillation boundary where pure ethanol is the stable node in one distillation region, in this instance, both steady states (and the third, unstable, steady state) are in the other distillation region (i.e. where pure ETBE is the stable node). The main effect of the ethanol-ETBE azeotrope is to increase the curvature of the distillation lines in the vicinity of the azeotrope. There is no evidence to suggest that the azeotrope causes the multiplicity.

The two steady states arise since the additional production rate of ETBE which results from maintaining an adequate supply of ethanol to the reaction zone can exactly balance the flow of ethanol that would otherwise leave the column with the bottoms product. That is, there is a singularity in the relationship between the bottoms mass flow and the bottoms molar flow. This is fully consistent with the fundamental explanation given in Section 8.2.1.

## 8.3 PSEUDO-MULTIPLICITY

### 8.3.1 Definition and Description

The concept of pseudo-multiplicity is proposed here to describe the difference between output multiplicity that is physically realisable and that which is not. Essentially, pseudo-multiplicity arises where multiple steady states are observed for a system which is described in molar units (which have no practical significance as a molar flow controller cannot be implemented in practice) but not in mass or volumetric units.

Several examples of pseudo-multiplicity in reactive distillation have been reported in the literature although they have not been described as such (e.g. Hauan et al., 1995; Schrans et

al., 1996). Importantly, these examples have been reported as output multiplicities and the fact that they are not physically realisable has been overlooked. This creates a false sense of the significance of these results and has, perhaps, contributed to the delay in providing experimental verification for multiplicity in hybrid reactive distillation.

Figure 8.14 shows pseudo-multiplicity in the 10 stage ETBE column which was introduced in Chapter 3 (Section 3.4). Some values of the reflux rate correspond to multiple steady state solutions with the same value of the molar boilup rate but only one steady state was observed for every reflux rate where a reboiler duty specification was applied (see Figure 4.3).

The 17 stage MTBE column described in Table 8.2 also exhibits pseudo-multiplicity. Figure 8.15 was constructed from simulation results with a molar bottoms rate of 674 kmol/hr (both parts of the curve satisfy this condition). Three steady states are seen for reflux rates above 900 m<sup>3</sup>/hr. However, if the bottoms rate is fixed with a mass or volumetric specification, only one steady state is observed for all values of the reflux rate (see Figure 8.2).

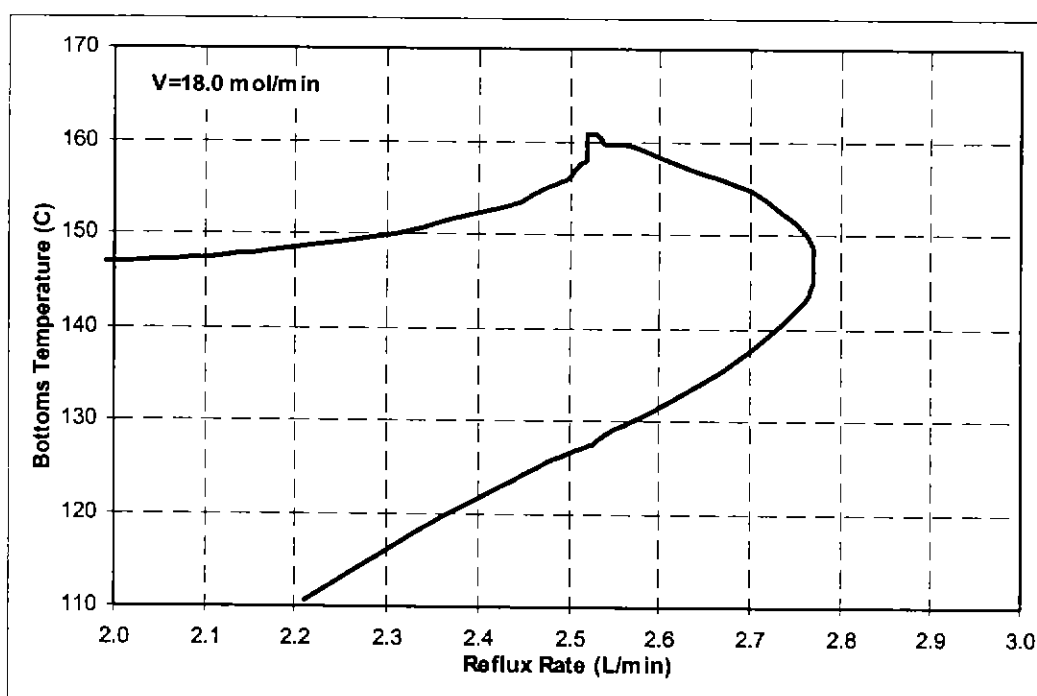


Figure 8.14 - Pseudo-Multiplicity in the 10 Stage ETBE Column

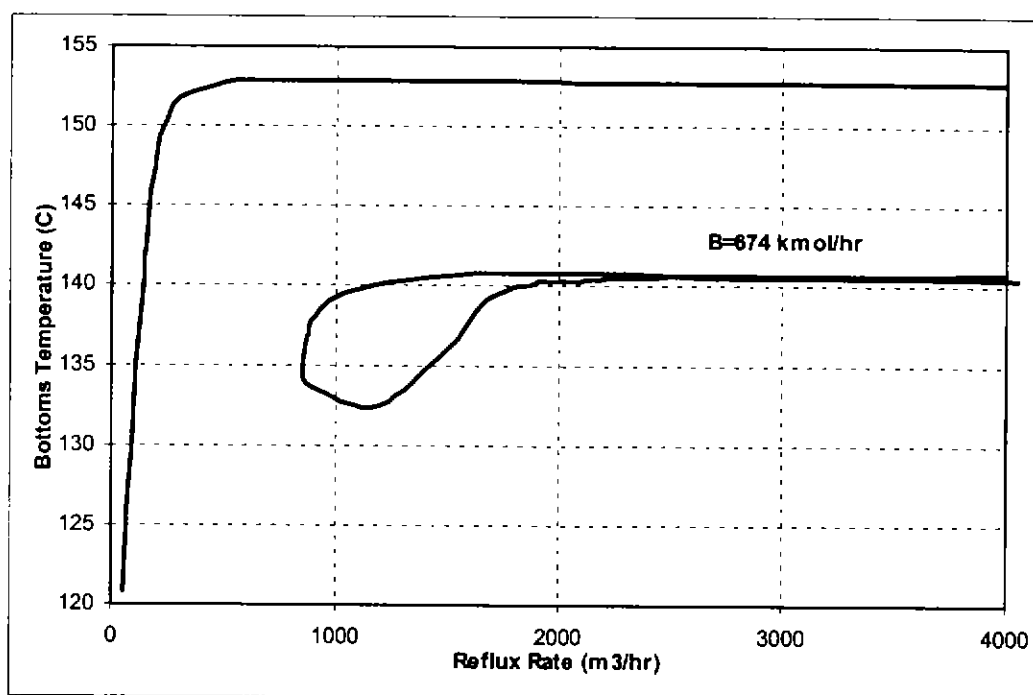


Figure 8.15 - Pseudo-Multiplicity in the 17 Stage MTBE Column

### 8.3.2 Source of Pseudo-Multiplicity

Mass-molar singularities are responsible for pseudo-multiplicity and sufficient conditions for pseudo-multiplicity are found from the inverses of equations (8.4) and (8.5).

$$\left( \frac{\partial B}{\partial B_m} \right) = 0 \quad (8.14)$$

$$\left( \frac{\partial V}{\partial Q_R} \right) = 0 \quad (8.15)$$

Equations (8.6) and (8.7) are also sufficient for pseudo-multiplicity if they are evaluated in molar units. If mass or volumetric units are used, the conditions are sufficient for physically realisable multiple steady states.

The transformation mechanism (from one steady state in realisable units to multiple steady states in molar units) is demonstrated in Figures 8.16 and 8.17, which pertain to the pseudo-multiplicities shown in Figure 8.14 and 8.15, respectively. In each case, the locus of points that satisfy the molar constraint comprises two or more points from the curves for realisable constraints. Since the molar constraints and the realisable constraints intersect at more than one point, there must exist points that satisfy equation (8.14) (Figure 8.17) and equation (8.15) (Figure 8.16).



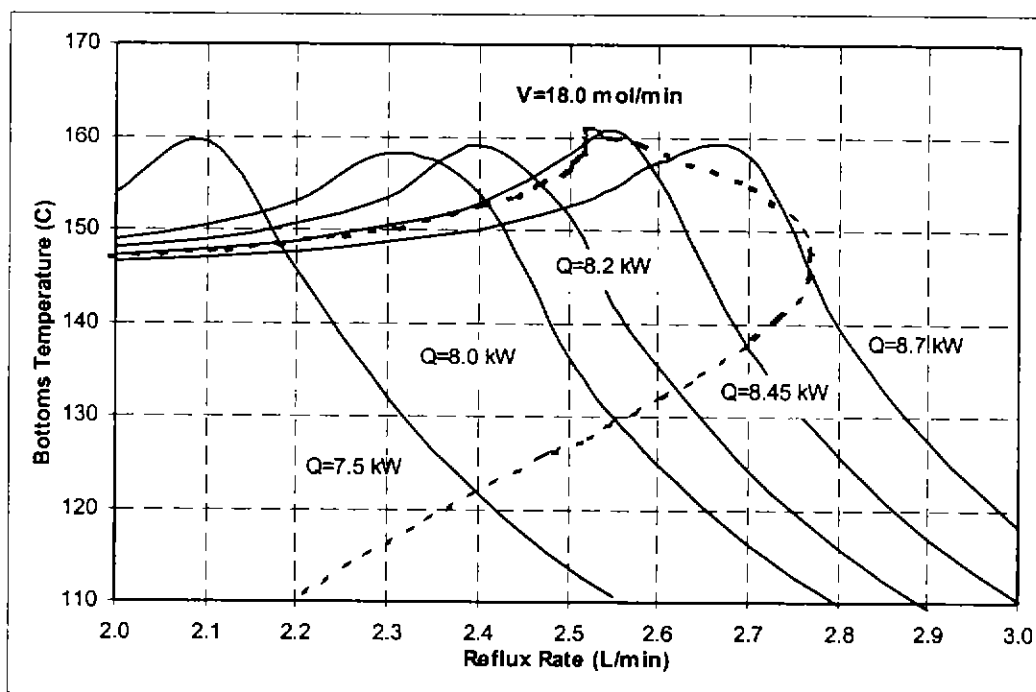


Figure 8.16 - Molar Boilup-Reboiler Duty Transformation in the 10 Stage ETBE Column

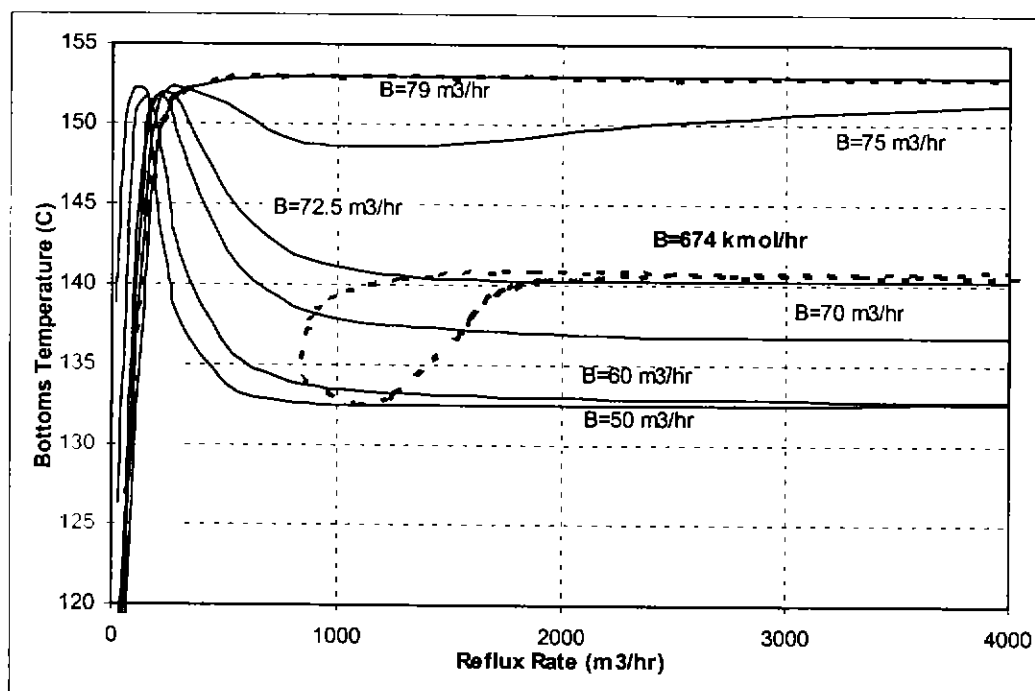


Figure 8.17 - Bottoms Rate Transformation in the 17 Stage MTBE Column

Jacobsen and Skogestad (1991) conjectured that output multiplicity was only likely for internal specifications. Recent results (e.g. Schrans, 1996) create doubt in this hypothesis as multiple steady states were reported for fixed bottoms rates in hybrid reactive distillation. However, these results were only obtained by assuming an unrealisable condition (e.g. a constant molar flow) so that the original conjecture remains sound and convincing.

## 8.4 ANALYSIS OF A COLUMN FOR MULTIPLE STEADY STATES

*A priori* knowledge of the likelihood for multiple steady states in the operation of a column will be valuable for the process operators. An understanding of the cause of any multiplicities will also help to avoid or manage operating difficulties that arise and help to define the conditions that lead to multiple steady states.

The principal tool for analysing columns for multiple steady states is the bifurcation study. Bifurcation diagrams are constructed by determining the steady state solution defined by fixing one operating parameter at a constant value and varying another parameter between the values that correspond to nil distillate and nil bottoms. The requisite data can be generated with any simulation model and the resulting data set can be plotted against any variable, in molar, mass or volumetric units. Many simulations could be required to fully define the bifurcation curve where complex behaviour is present (e.g. approximately 70 points needed for Figure 8.9) but these can be completed relatively quickly with advanced simulation tools.

It is desirable to complete bifurcation studies with a rigorous model and with a CMO model, and to prepare bifurcation diagrams in both molar and mass units in order to determine the principal cause of any observed multiplicities. There is no physical significance to the simulations completed with either the CMO model or with constant molar flow rates since both of these cases are based on incorrect assumptions (i.e. constant molar overflow, and a one-one relationship between molar flows and mass or volumetric flows). However, the comparison of all four sets of results points to the fundamental cause of the multiplicity and this could provide further insight into the physical process.

Table 8.5 indicates how the bifurcation results should be collectively interpreted. Cause I refers to unit singularities, cause II refers to energy balance multiplicities, cause III refers to the azeotropic mechanism and cause IV is reaction hysteresis. These results also provide the data necessary to determine whether multiple steady states are physically realisable or due to a pseudo-multiplicity: this distinction has significant implications for the operation and control of the process.

Table 8.5 - Types and Causes of Multiplicity

Multiple Steady States Detected?					
<u>Model includes energy</u> <u>balances</u>		<u>CMO case</u>		<u>Cause</u>	<u>Type</u>
<u>Molar units</u>	<u>Mass units</u>	<u>Molar units</u>	<u>Mass units</u>		
x	✓	x	✓	I	real
✓	x	✓	x	I	pseudo
✓	✓	x	x	II	real
x	✓	x	x	II	real
✓	x	x	x	II	pseudo
✓	✓	✓	✓	III or IV	real

The distinction between multiplicity due to azeotropes and reaction hysteresis is best made using the reactive  $\infty/\infty$  technique (Güttinger and Morari, 1997). Simulations are not required and, where an  $\infty/\infty$  analysis has been completed previously (e.g. the MTBE analysis appears in the literature), only the feed composition in transformed coordinates is required to determine whether multiple steady states are possible. However, as indicated previously, there is uncertainty in the results of an  $\infty/\infty$  analysis for finite columns and hybrid columns, and the analysis is only applicable for internal specifications. Nevertheless,  $\infty/\infty$  predictions are frequently accurate and the technique is useful to eliminate azeotropes as a possible source of multiple steady states.

## 8.5 TRANSITIONS BETWEEN PARALLEL STEADY STATES

### 8.5.1 Open-Loop Transitions in a MTBE Column

The effects of various perturbations on the 17 stage MTBE column described in Table 8.1 were investigated via a series of dynamic simulations. The column was assumed to be operating in open-loop mode with the reflux rate and reboiler duty constant. Figure 8.9 indicates that there are three steady state solutions (i.e. high, low and medium conversions) with this set of input conditions, and the responses of the column were found separately from each steady state. The reboiler temperature was used to determine how the column responded to the various perturbations for each of the simulations.

#### 8.5.1.1 Transitions from the High Conversion (Stable) Steady State

Initially, the effects of perturbations in the feed composition were investigated. Starting with stable operation at the high conversion steady state, various increases and decreases in the methanol feed rate of 10% and 15% over 30, 60 and 120 minutes were considered. The

column returned to the initial operating point without significant perturbation from the original condition in most cases. Numerical errors associated with rapid changes in state variables produced incomplete solutions in the other cases, possibly indicating an instability caused by a depletion of liquid in one part of the column. There was no evidence of a transition to another steady state for any of the perturbations considered. Figure 8.18 plots the column responses for a 10% increase in the methanol feed rate over 120 minutes (solid line) and a 10% decrease over 60 minutes (dashed line). Interestingly, a 10% decrease in the methanol feed rate for 60 minutes had almost no effect on the column while a 10% increase for 120 minutes substantially changed the bottoms temperature for a considerable period. These responses clearly show highly non-linear behaviour, which is a characteristic of many distillation processes.

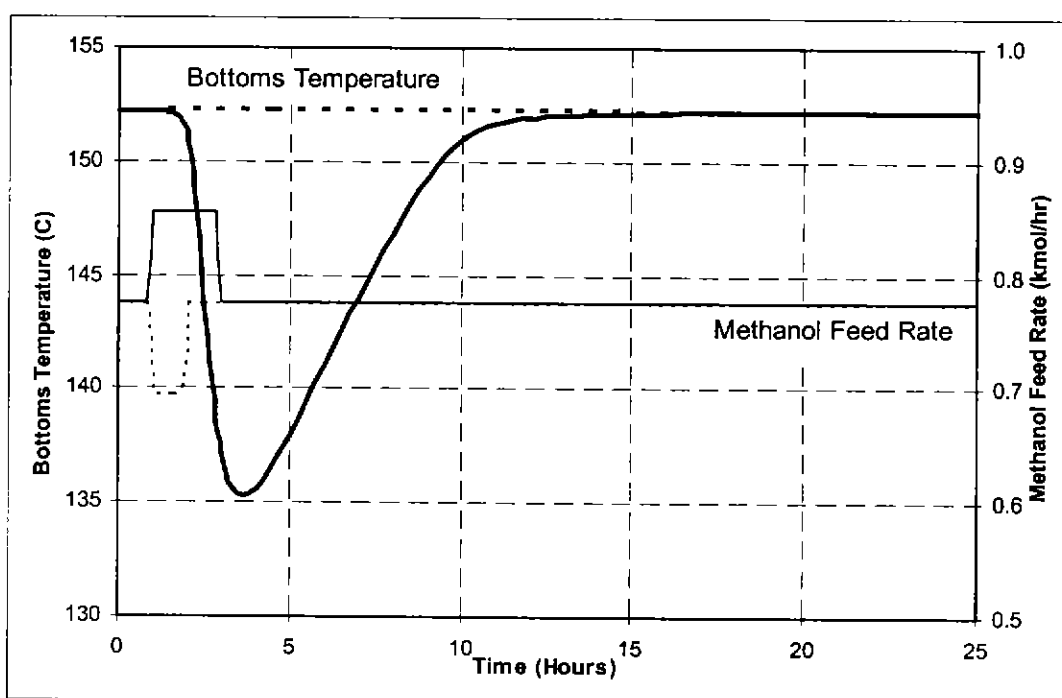
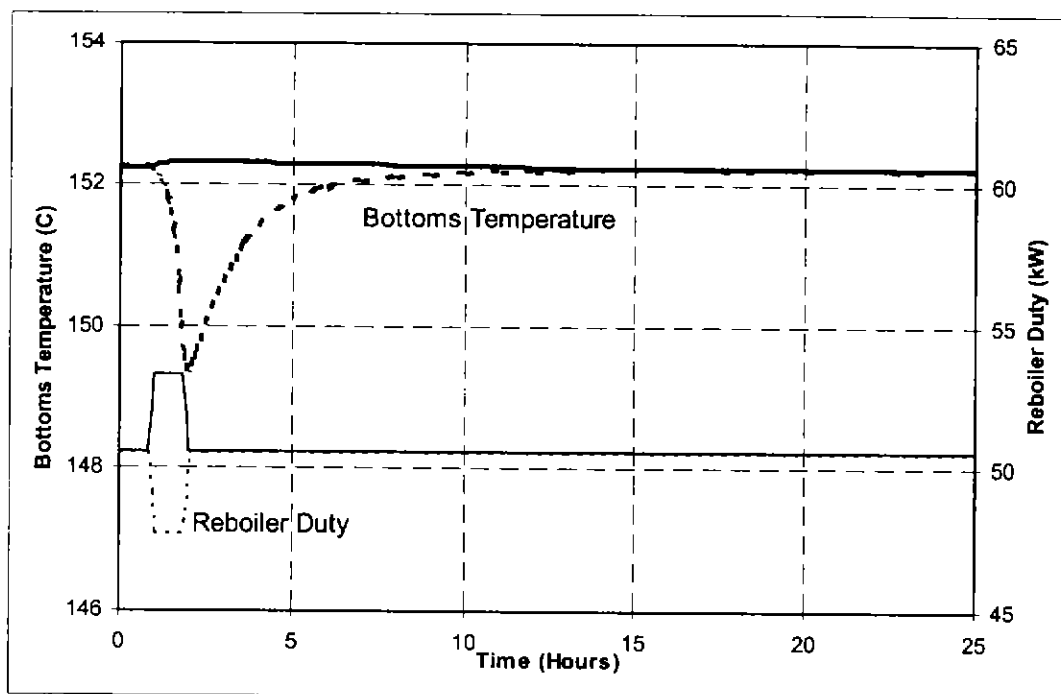


Figure 8.18 - 10% Methanol Feed Rate Changes from the High Conversion Steady State

Disturbances in the reboiler duty were also considered. In these simulations, the feed rate, feed composition and reflux rate were all fixed, while the reboiler duty was varied by  $\pm 5\%$  over 30 minutes and 120 minutes (four different cases). In three of the four cases, the column returned to the initial operating point quickly and smoothly, while a 5% increase over 120 minutes caused the column flows and temperature to oscillate divergently. The response to a 30 minute increase and decrease is shown in Figure 8.19. As would be expected, a much greater deviation from the initial conditions is observed for longer perturbations in the reboiler duty.



**Figure 8.19 - 5% Reboiler Duty Changes from the High Conversion Steady State**

The results presented above suggest that the high conversion steady state is locally stable. Neither perturbations in the feed nor in a primary manipulated variable (i.e. reboiler duty) produced a steady state transition. This result is important as it implies that column operation should be stable once the high conversion steady state has been attained. This reduces the implications of steady state multiplicity for the operation of this MTBE column. However, it does not eliminate the possibility of a start-up sequence ending with the column in an undesirable steady state nor does it eliminate the possibility of an unstable high conversion steady state in other columns.

#### *8.5.1.2 Transitions from the Low Conversion (Stable) Steady State*

A similar series of tests was simulated starting from the low conversion steady state. The methanol feed rate was increased and decreased by 10% over 120 minutes. In both cases, the column settled to the original operating point. However, if the methanol feed rate was temporarily increased or decreased by 15% over the same period, the column jumped to the high conversion solution! The response to a 15% increase is shown in Figure 8.20. Steady state transitions were not detected for perturbations in the reboiler duty although relatively small increases (e.g. +3% over 30 minutes) caused the reboiler sump to dry up and destabilise the column. Similarly, relatively small decreases in the reboiler duty increased the internal column liquid rate significantly and induced flooding.

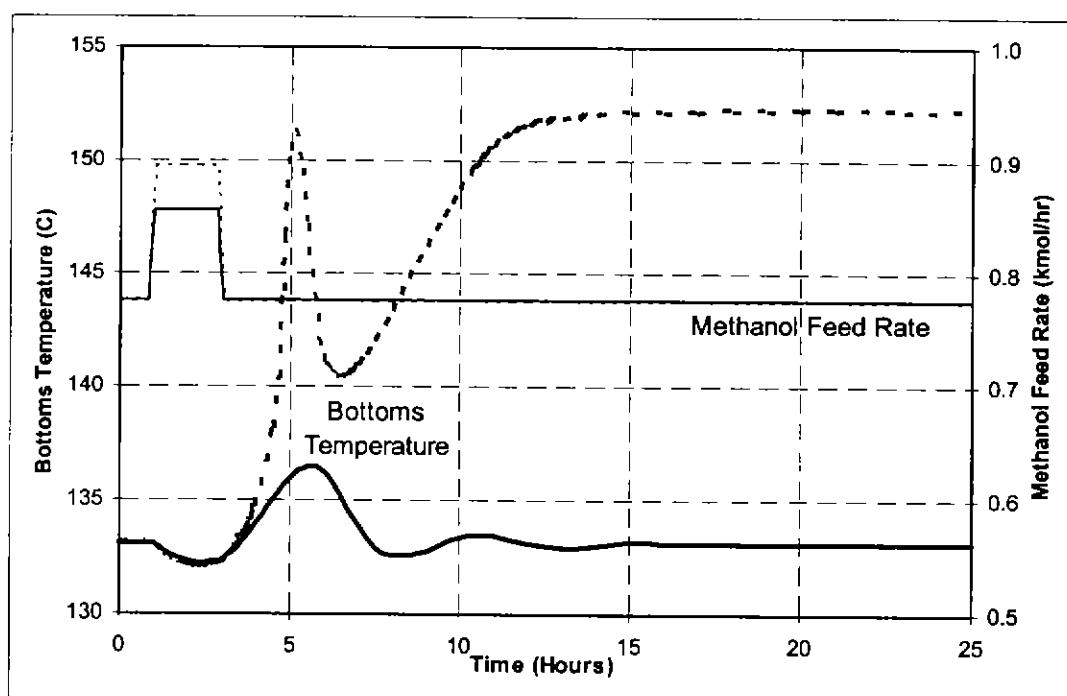


Figure 8.20 - 10% and 15% Methanol Feed Increases from the Low Conversion Steady State

#### 8.5.1.3 Transitions from the Medium Conversion (Unstable) Steady State

Starting from the medium conversion steady state, several unusual results were found. Firstly, every perturbation that was considered produced a steady state transition. This is emphasised in Figure 8.21, which indicates that a steady state transition occurs after a short, temporary increase of only 1% in the reboiler duty. Secondly, the column could shift to either the high or low conversion steady state. Figure 8.22 indicates the effect of a 10% and a 15% increase in the methanol feed rate and shows that the column stabilised to the low conversion steady state in the first case (10% perturbation) and the high conversion steady state in the second case (15% perturbation). Thirdly, some transitions were very smooth and had been fully manifested within 120 minutes while some transitions took more than 15 hours. An example of this is given by Figure 8.23, which indicates the response to a perturbation of  $\pm 5\%$  in the methanol feed rate. The response to a 5% decrease was rapid while a 5% increase initiated a transient response that lasted for several hours.

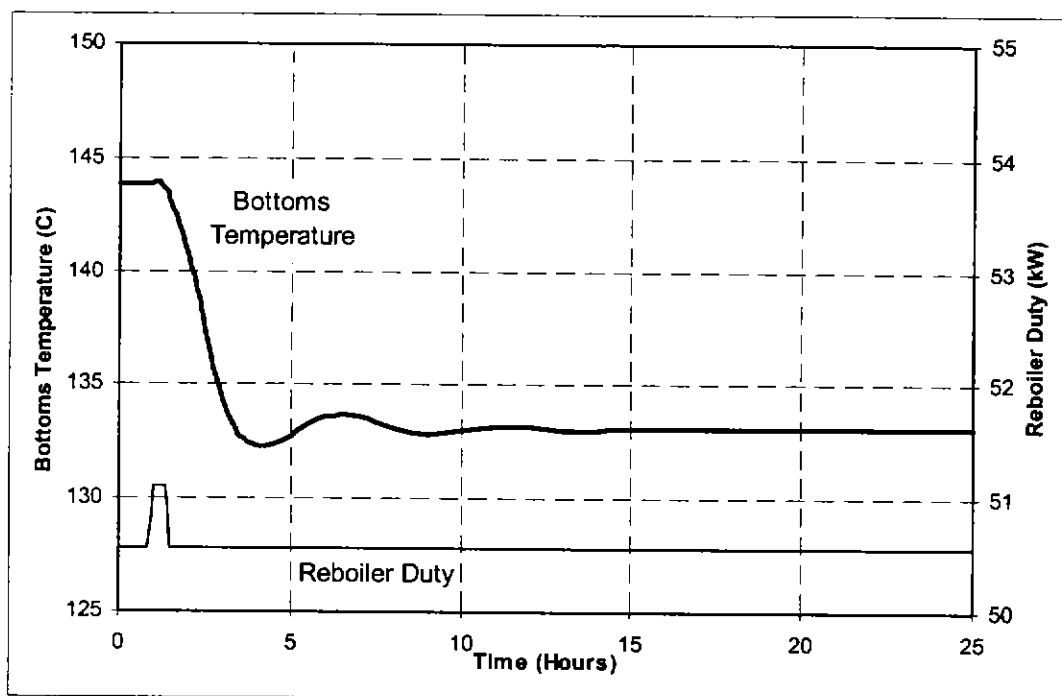


Figure 8.21 - 1% Reboiler Duty Increase from the Medium Conversion Steady State

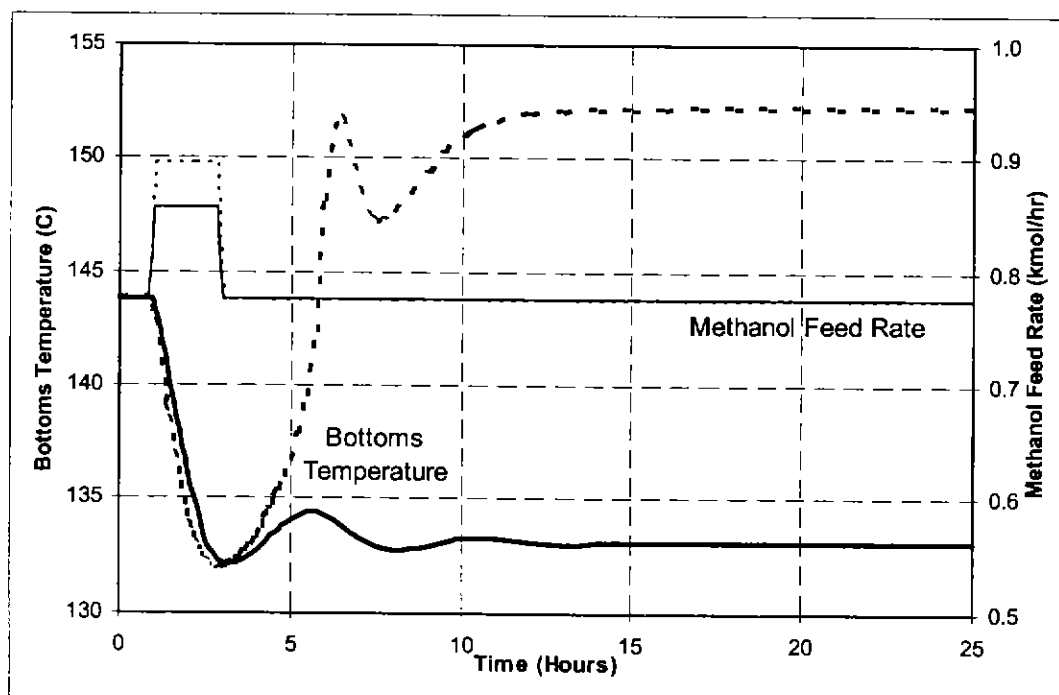


Figure 8.22 - Methanol Feed Rate Increases from the Medium Conversion Steady State

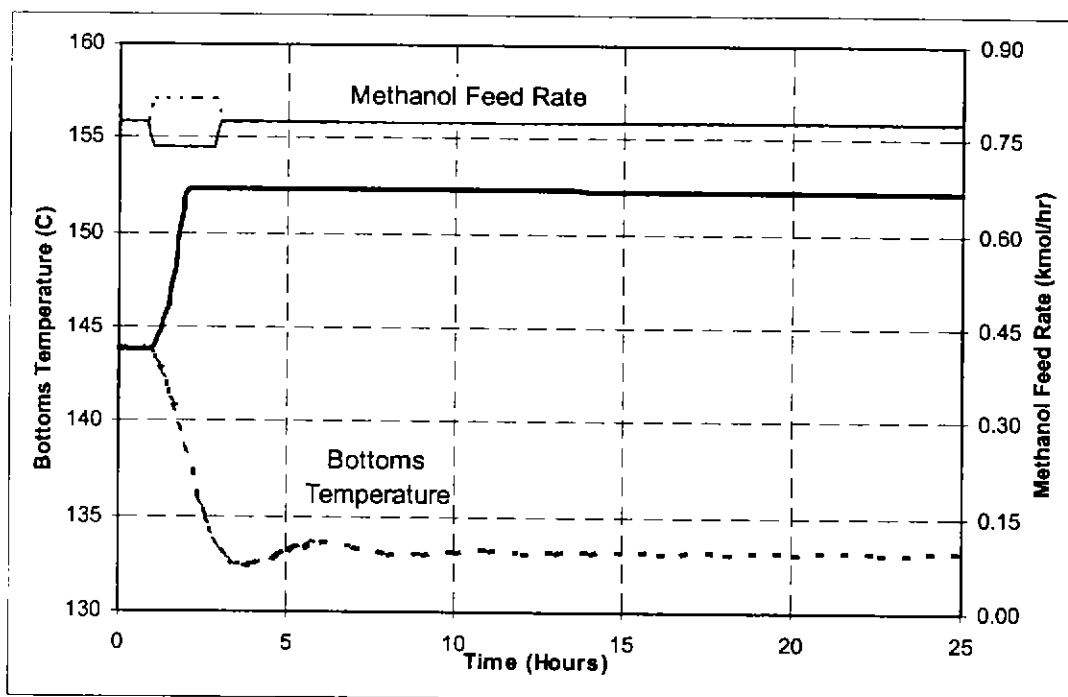


Figure 8.23 - 5% Methanol Feed Rate Changes from the Medium Conversion Steady State

Fourthly, slight changes in the initial operating point sometimes resulted in completely different column responses. Figure 8.24 compares the response to a 10% increase in the methanol feed rate from two slightly different initial conditions. The solid line corresponds to the same base case as used for all the previous simulations (reboiler duty of 50.6 kW) while the dashed line shows the response for a reboiler duty of 50.0 kW with all other variables equal. Note that the initial bottoms temperature shifts from 144°C to 141°C due to the difference in the column energy balance. The column shifted from the medium conversion steady state to the high conversion steady state when the reboiler duty was 50.0 kW whereas it shifted to the low conversion steady state when the initial operating point equated to the original base case (50.6 kW).



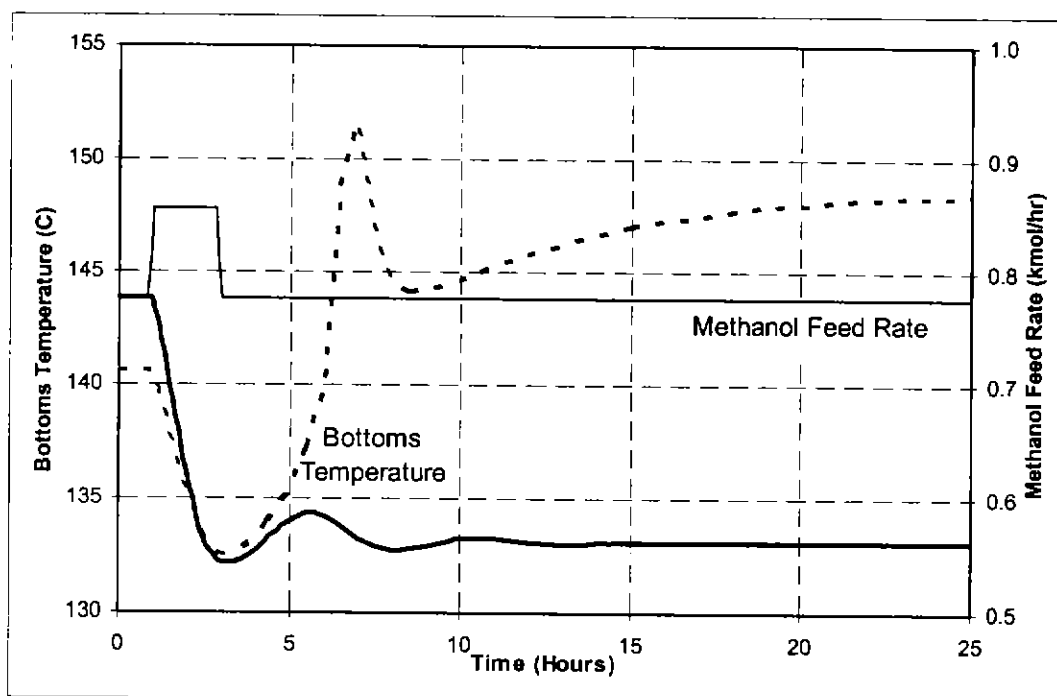


Figure 8.24 - 10% Methanol Feed Increase from Similar Medium Conversion Steady States

### 8.5.2 Closed-Loop Transitions

Steady state transitions are clearly possible for a range of realistic disturbances when open-loop operation is considered. Are transitions still possible if closed-loop control is used? Output multiplicity implies that there is more than one set of output variables which satisfy a single set of inputs. If each set of outputs are separate and distinct, perfect control of any output variable will confine the column to a single steady state for any known set of inputs. However, if the parallel output sets have common elements, control of one of those common elements might not be sufficient to prevent a transition to a parallel steady state. Therefore, the choice of appropriate controlled variable(s) within the control scheme is paramount.

The selection of controlled and manipulated variables is discussed extensively in Chapters 9 and 10. However, four variable pairings are considered here to demonstrate the importance of making effective choices where steady state transitions must be avoided. Figure 8.25 shows the relationships between the reboiler temperature,  $T_b$ , and the temperature on stage 12 (i.e. top of the stripping section),  $T_{12}$ , and the reboiler duty. Figure 8.26 examines the relationships between  $T_b$  and  $T_{12}$  and the bottoms draw rate. The points designated A, A', B and B' correspond to the same operating conditions in Figures 8.25 and 8.26.

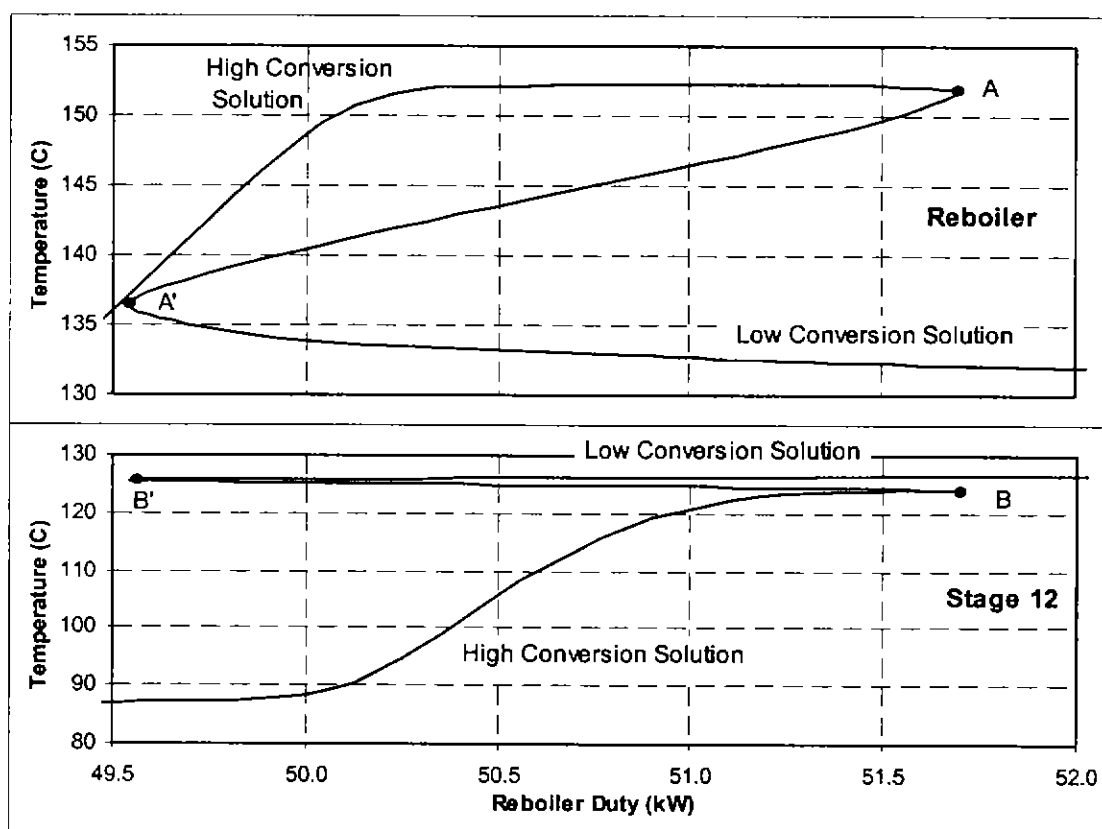


Figure 8.25 - Relationships Between Reboiler Duty and Column Temperatures

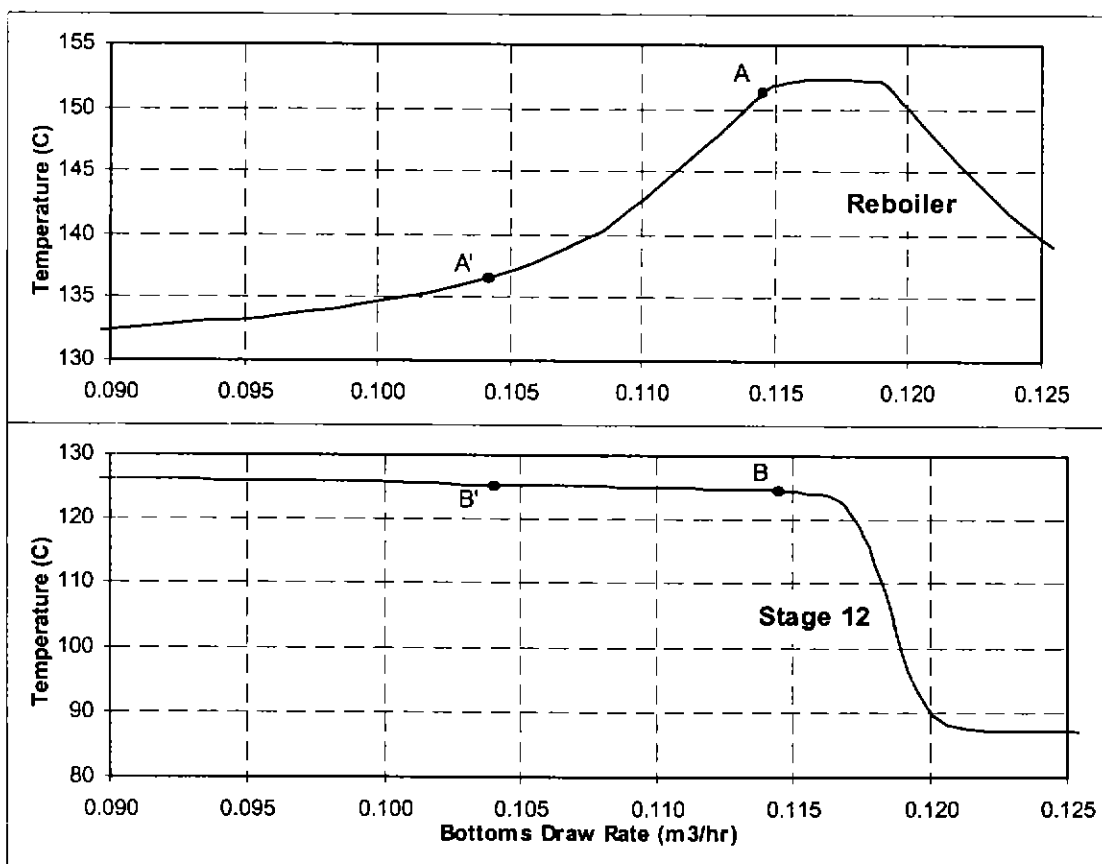


Figure 8.26 - Relationships Between Bottoms Rate and Column Temperatures

The upper part of Figure 8.25 indicates the variation in  $T_b$  with the reboiler duty. The important aspect of this plot is that most values of  $T_b$  correspond to two separate values of the reboiler duty,  $Q_R$ . In contrast, the lower part of Figure 8.25 shows that each value of  $T_{12}$  corresponds to one (and only one) value of the reboiler duty. Therefore, the perfect control of  $T_{12}$  will confine the column to a single operating point (i.e. a single steady state) but control of  $T_b$  will not. Figure 8.26 shows that either  $T_b$  or  $T_{12}$  could be used in conjunction with the bottoms draw rate without risking an unwanted steady state transition. In fact, open-loop operation is sufficient to avoid a transition if the bottoms rate and the reflux rate are the variables which are fixed since only one steady state exists for all values of the bottoms rate. However, this analysis conceals that a linear controller for the reboiler sump level would be unstable as the sign of the gain is indeterminate between A and A' (or B and B'). This can be inferred from Figures 8.25 and 8.26 together: some values of the bottoms rate correspond to multiple values of the reboiler duty.

This analysis suggests that a linear controller using the pairing  $T_{12}$ - $Q_R$  is acceptable but the other three combinations are not. The  $T_{12}$ - $Q_R$  controller will prevent unwanted steady state transitions and simplify the associated inventory control system. However, a linear controller will be unstable for  $124.5^\circ\text{C} < T_{12} < 125.5^\circ\text{C}$  as the process gain is negative in this interval and positive elsewhere. The controller may also be inefficient for  $T_{12} > 125.5^\circ\text{C}$  (i.e. the low conversion steady state) because of tuning as the process gain is approximately 50 times lower than for  $T_{12} < 124.5^\circ\text{C}$  (i.e. the high conversion steady state and normal operating region).

A similar logic can be applied to more complex, multivariable controllers to determine if closed-loop control will necessarily prevent a steady state transition. Regardless of the type of controller, the key consideration is whether the controlled variables are common to multiple steady states. Two-point control would make a transition almost impossible since there must be two common elements in each output set (i.e. the values of both controlled variables).

In practice, reasonably tight control (but not necessarily perfect control) of almost any temperature within the column should be sufficient to prevent a steady state transition. This ensues from the differences between the temperature profile of the different steady states, particularly in the stripping section where the controlled variable is likely to be located. However, although tight control of any temperature is adequate, this might only be realisable for some temperatures. For example, the process gain,  $T_b$ - $Q_R$ , is both positive and

negative in the normal operating region (i.e. the high conversion steady state) so that a linear controller for this temperature could not be globally stable.

This result provides further encouragement that once the high conversion steady state is reached, the column operation should be stable, especially if closed-loop control is used. However, the possibility of a start-up sequence ending at an undesirable steady state still remains as start-up is almost always conducted in open-loop.

## **8.6 OPERABILITY ISSUES**

### **8.6.1 Equipment Selection**

The presence of input multiplicity in hybrid reactive distillation influences the optimal design and selection of equipment, particularly the reboiler. The performance of both the ETBE and MTBE systems is sensitive to the principal operating variables (e.g. Figure 4.3). There is only a narrow range of conditions where phase and chemical equilibrium intersect favourably to promote effective reaction and separation concurrently. Therefore, precise control of all the manipulated variables is required. This is readily attainable where a flow is controlled but restrictive in designing the reboiler. For example, integrated exchanger networks are desirable to conserve energy and minimise utility consumption but might not provide sufficient control over the reboiler duty. A fired heater permits more precise control but is more costly to operate. Therefore, there is a trade-off between operability, performance and cost.

Clearly, output multiplicity also affects the operability of hybrid reactive distillation columns. Unwanted transitions between parallel steady states could result in substantial production losses. In an extreme case, regular transitions could make a reactive column unworkable and result in a return to more conventional technology. Steady state simulations can be used to determine the potential benefits of using a hybrid column but they do not indicate whether the potential is realisable. If a complex and costly advanced control system is required to permit a hybrid column to operate effectively, or additional operating staff are required, the steady state benefit of utilising reactive distillation technology could be offset by increased operating costs and reduced flexibility, operability and reliability.

The need to reconcile operability and performance extends to other processes and many design modifications, particularly those directed at increasing integration between process

units. The present example suggests that it is crucial to consider the difference between a realisable benefit and a potential benefit in preparing a project justification.

### 8.6.2 Start-Up

The presence of output multiplicity and, therefore, hysteresis in some hybrid columns has significant implications for the start-up of those columns. Since the operating conditions at any time are a function of the process inputs and the history of the column, the start-up procedure can influence the steady state process performance. Some start-up procedures will culminate with the column operating at or close to the design conditions while other procedures will confine the column conditions to the low conversion solution branch.

Referring again to the 17 stage MTBE column, Table 8.6 shows two sets of steady state conditions for process inputs that could be found during a start-up. The column temperatures are close to the design basis in both cases and only the reboiler duty needs further adjustment to match the targets. In the first case (A in Table 8.6), the reboiler duty must be decreased by approximately 3% while in the second case (B) the duty must be increased by the same amount to reach the design conditions. A comparison of the temperature profiles in cases A and B with the design targets suggests that case A would provide the fastest route to the design point since many of the temperatures are already close to the desired values.

The steady states given by cases A and B were disturbed by making the requisite changes in the reboiler duty to attain the design targets. The transient responses are shown in Figures 8.27 (case A) and 8.28 (case B). Although start-up A settles more quickly than start-up B, it converges to a low conversion steady state. Start-up B is considerably slower but is effective in attaining the design basis conditions. Figure 8.29 shows the various steady states on a bifurcation diagram of the column with a constant volumetric reflux rate (i.e.  $1.20 \text{ m}^3/\text{hr}$ ) and clearly explains the observed behaviour. The output multiplicity creates restrictions on the start-up procedure that are not present for columns that do not exhibit this phenomenon.

Table 8.6 - Steady State Conditions Found During Two Start-Ups

	Design Basis	Start-Up A	Start-Up B
<i>Operating Conditions</i>			
Hydrocarbon feed composition	36% isobutene, 64% n-butane	36% isobutene, 64% n-butane	36% isobutene, 64% n-butane
Methanol excess (mol%)	10.0	10.0	10.0
Reflux rate (m <sup>3</sup> /hr)	1.20	1.20	1.20
Reboiler duty (MW)	50.6	52.2	49.0
<i>Temperature Profile (°C)</i>			
Condenser	81	80	81
Mid-reactive section	95	99	84
Feed stage	112	112	86
Mid-stripping section	130	130	87
Lower stripping section	132	132	91
Reboiler	152	132	122

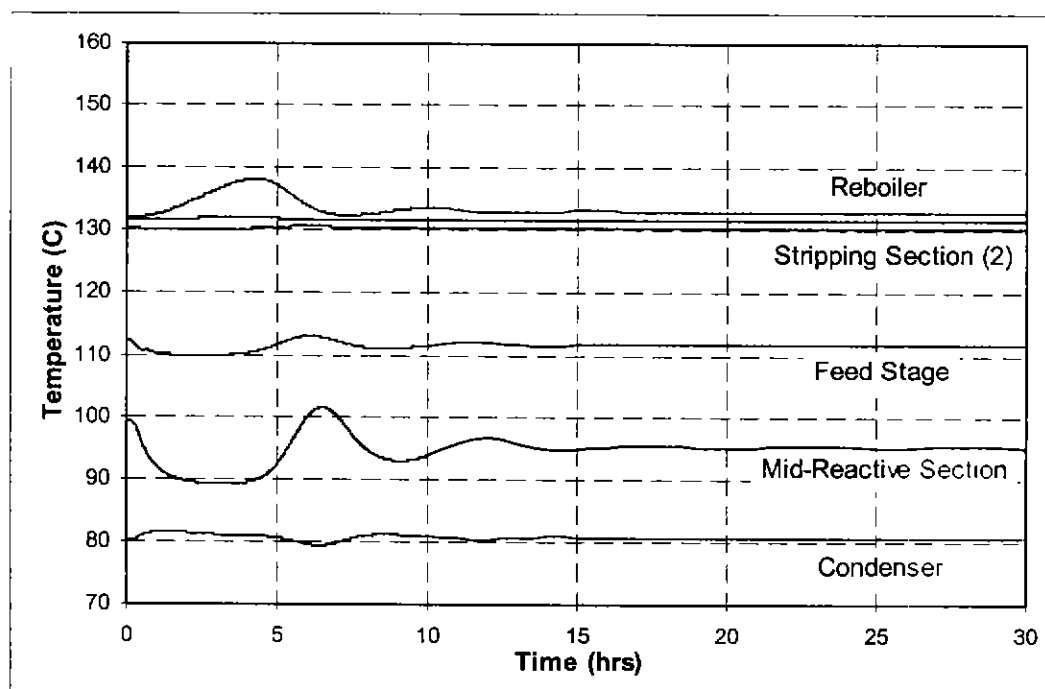


Figure 8.27 - Transient Response to a Decrease in Reboiler Duty to the Target (Start-Up A)

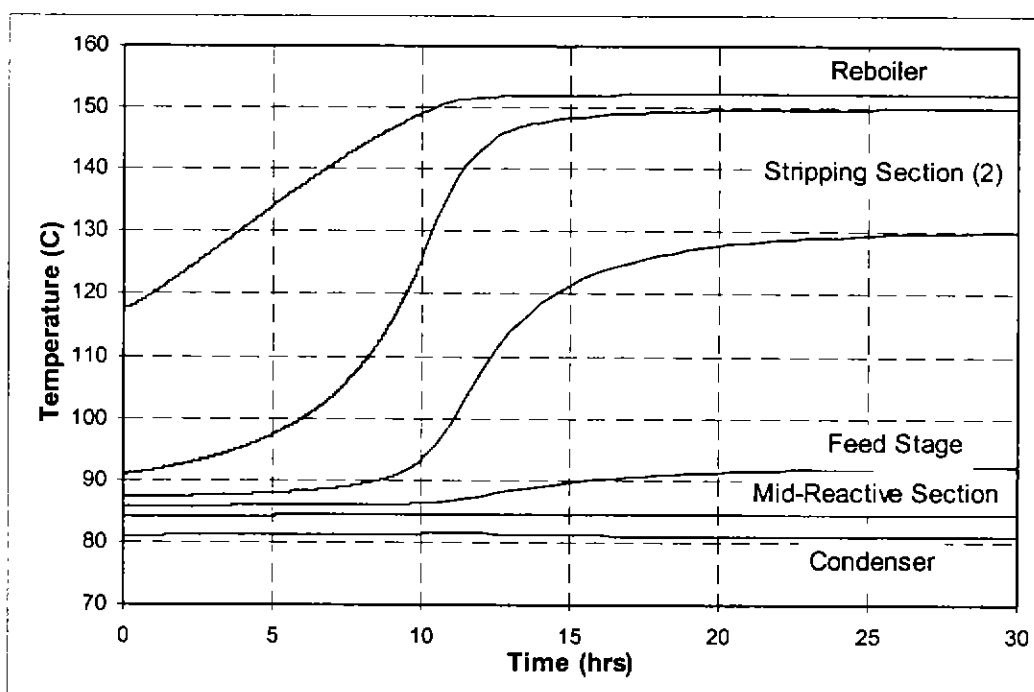


Figure 8.28 - Transient Response to an Increase in Reboiler Duty to the Target (Start-Up B)

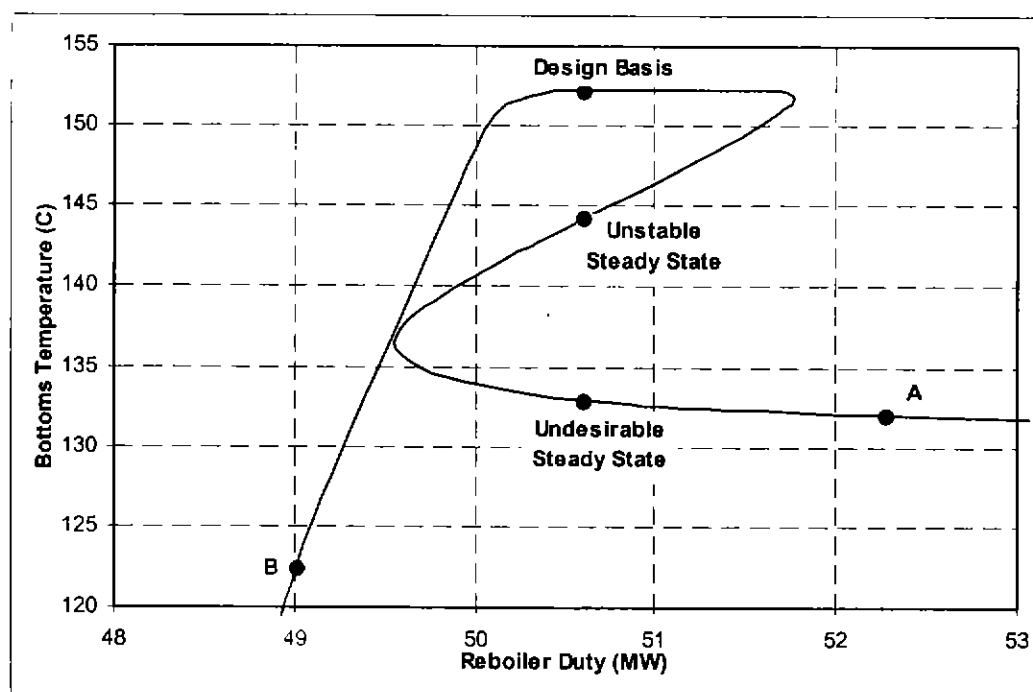


Figure 8.29 - Start-Up Restrictions Predicted by the Bifurcation Diagram

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## **CHAPTER NINE**

### **CONTROL ISSUES I - OPEN-LOOP AND ONE-POINT CONTROL**

- 9.1 Basic Process Objectives**
- 9.2 Degrees of Freedom Analysis**
- 9.3 Open-Loop Control**
- 9.4 One-Point Control**
  - 9.4.1 Applicability of One-Point Control
  - 9.4.2 Control Objective
  - 9.4.3 Control Configuration

#### **9.1 BASIC PROCESS OBJECTIVES**

The final, overall objective of any process control application should always be to maximise the profitability of the process under control. This is normally achieved via a rationalisation of the value added by the process with the energy that is consumed by the process. For example, in a conventional distillation column, increasing the internal vapour and liquid flows nearly always increases the separation of key components and, therefore, increases either the product yield or its value. However, the increase in internal flow rates is only achieved at the expense of additional energy consumption in both the condenser and reboiler. With most reactors and many other unit operations, this principle often manifests itself with respect to the heating or cooling requirement, or the recycle rate. An effective control application adjusts the process operation towards an optimum where the incremental value added is just less than the incremental cost of the energy and raw materials.

Reactive distillation combines the functionality of both the reaction and purification stages of a process and the main operating objective for a reactive distillation column should reflect both roles. The conversion of lower value reactants to higher value products is the facet of reactor operation that contributes value to a process and this is usually best measured via the molar conversion of the limiting reactant. The effectiveness of a distillation process can be measured via a separation factor, which relates the purity of the top and bottoms products (e.g. equation 9.1).

$$S = \frac{x_{H,B} B}{z_H F} \times \frac{x_{L,D} D}{z_L F} \quad (9.1)$$

The overall benefit of a reactive distillation process arises from both the conversion of reactants and the separation of products. Therefore, an appropriate metric for reactive distillation should combine both measurements (e.g. equation 9.2).

$$V = X \times S \quad (9.2)$$

The conversion of the limiting reactant,  $X$ , and the separation factor,  $S$ , are both bounded between 0 and 1. Therefore, the reactive distillation metric,  $V$ , will also be bounded between 0 and 1. Presumably, the value of  $V$  will increase with the energy consumed by the process so that a minimisation problem can be constructed to determine the optimal operating conditions. However, it will usually not be possible to show that the minimisation problem is convex, and several results from Chapters 4 to 6 suggest that  $V$  might not always increase monotonically with energy consumption. Therefore, an alternative formulation of the process objective(s) is warranted.

This can be achieved by considering the process and operating constraints. The product value from any chemical process is rarely a smooth function of its properties. Instead, the product will often have a constant value provided that its properties are between certain limits or specifications. Under these conditions, the maximum value from the process is often obtained at the coincidence of two or more constraints. For example, the profitability of a reactive ETBE column might be maximised when *isobutene conversion is maximised and ETBE losses (in the distillate) are minimised whilst maintaining the ETBE product purity between specification limits*. The process objectives arising from this statement are:

- a) maximum isobutene conversion;
- b) minimum ETBE in the distillate;
- c) ETBE purity in the bottoms maintained at a designated value.

With different economic circumstances, the value added by the process coupled with high demand for the product will be more significant than the incremental energy cost and there is an incentive to operate the system to maximise throughput up to the equipment constraints while maintaining product quality at the minimum acceptable value. For example, the value of ETBE (compared with the raw materials and energy) might be such that throughput is a more important consideration than both the isobutene conversion and any loss of product in the distillate. The requirements for maximum profitability in this

situation are *maximum throughput whilst maintaining the ETBE product purity between specification limits*. The specific process objectives would then be expressed as:

- a) maximum bottoms draw rate;
- b) ETBE purity in the bottoms maintained at a designated value.

Whatever the operating objectives are determined to be (and they will vary depending on the economic circumstances and other external factors), the controller design should focus on these criteria. It should be noted, however, that it might not be possible to satisfy all of the process objectives simultaneously.

## 9.2 DEGREES OF FREEDOM ANALYSIS

A simple two-product distillation column with a single feed and a total condenser has five degrees of freedom. These correspond to control valves that vary the following quantities:

- the distillate product draw rate (D);
- the bottoms product draw rate (B);
- the reboiler duty ( $Q_R$  or  $V$  to denote the internal vapour rate);
- the reflux rate (L for the internal liquid rate);
- and the condenser duty ( $Q_C$ ).

The condenser and reboiler duties usually cannot be manipulated directly but the designations,  $Q_R$  and  $Q_C$ , are used to represent the group of variables which could be used to adjust the duty in each case. For example, the control valve which is designated to regulate the condenser duty might actually manipulate the coolant flow rate (either directly or indirectly by regulating the bypass rate), the active surface area of the condenser or the rate at which vapour is withdrawn from the column. Similarly, the method of regulating the reboiler duty could be the heating medium flow rate, the reboiler exchanger area or the process flow through the reboiler.

The column pressure, the reboiler sump level and the reflux accumulator level (i.e. the column vapour and liquid inventory) must all be stabilised for the column to operate in a steady-state. The column pressure is almost always controlled via the condenser duty (Luyben, 1992) and tight control is usually achievable with a simple SISO control loop. The liquid inventory can usually also be controlled by two simple SISO controllers provided either the distillate rate or the reflux rate is used to control the reflux accumulator level and either the bottoms rate or the reboiler duty is used to control the reboiler sump level.

Therefore, two degrees of freedom remain for the control of the process objectives. If neither of these variables is used within a control loop (i.e. the process operator manipulates the control valves directly), the column is said to be operated in open-loop or manual. If only one of these variables is manipulated automatically to control a measured property, a one-point or single composition control scheme is deemed to be in use. In this case, the remaining degree of freedom is usually fixed at a constant value or manipulated only occasionally to reflect capacity constraints (e.g. maximum reboiler duty or flooding). Finally, both available degrees of freedom can be utilised within control loops. This is known as two-point or dual composition control.

### 9.3 OPEN-LOOP CONTROL

The most basic distillation control system considers only the column inventory and relies on the process operator to counteract disturbances to the process by adjusting (when required) one or both of the manipulated variables which are not being used for inventory control. The effectiveness of this approach depends on the variable pairings (i.e. the control configuration).

It is convenient to adopt a nomenclature to concisely describe the variable pairings or control configuration. The most widely accepted method of describing control configurations employs two letter designations that correspond to the variables which are *not* used for inventory control. For example, the LV configuration uses the distillate product draw rate (D), the bottoms rate (B) and the condenser duty ( $Q_c$ ) to control the reflux accumulator level, the reboiler sump level and the column pressure, respectively.

The requirement for dynamic responsiveness in the inventory control loops (as described in Section 9.2) restricts the number of acceptable control configurations. Effectively, one of the distillate rate and reflux rate and one of the bottoms rate and reboiler duty must be used for inventory control. Thus, only four pairs of manipulated variables are suitable: LV, DV, LB and DB. Of these, the DB configuration cannot be used in open-loop as the two manipulated variables are not independent at steady state because of the column material balance. Ratios and other linear combinations of the manipulated variables can also be considered so that many more control configurations are made available. The (L/D)V configuration (also known as Ryskamp's scheme: Ryskamp, 1980) and the (L/D)(V/B) or double ratio configuration are prominent among the ratio control schemes. Ratios involving the feed rate (F) are also possible, for example, the (D/F)V configuration which effectively incorporates steady state feed-forward control into the control structure.

Every control structure has the capability to reject (or attenuate) certain disturbances without requiring the intervention of the process operator. For example, in ideal binary distillation where the constant molar overflow assumption applies, constant vapour and liquid loadings (i.e. constant reflux rate and reboiler duty) presupposes constant fractionation. Therefore, if the feed rate increases, the product compositions will change only very slightly if no corrective action is taken. Similarly, if the column material balance is fixed via one of the product draw rates, at least one of the product compositions will remain close to its initial value following small changes in the feed composition without any change in the manipulated variables.

The open-loop disturbance rejection of several control structures were determined for the 10 stage ETBE hybrid reactive distillation column described in Chapter 3 using the SpeedUp™ dynamic simulation model. The results from this study are shown in Table 9.1 and indicate that only the double ratio configuration provided effective rejection of feed rate disturbances and that only the (L/D)V configuration was effective against feed composition disturbances. This is not surprising considering the narrow range of acceptable operating conditions predicted in Chapter 4. In practice, none of the control structures that were examined could be used successfully in open-loop operation of the ETBE column without regular intervention from the process operator. This suggests that some form of closed-loop composition control will always be required.

Table 9.1 - Open Loop Gains for Feed Rate and Feed Composition Disturbances

	<b>Feed Rate Disturbance</b>	<b>Feed Composition Disturbance</b>
<b>LV</b>	-3.6°C / % feed rate	-0.45°C / % excess
<b>DV</b>	-3.8°C / % feed rate	+0.50°C / % excess
<b>LB</b>	+2.6°C / % feed rate	-6.7°C / % excess
<b>(L/D)V</b>	-3.4°C / % feed rate	-0.01°C / % excess
<b>(L/D)(V/B)</b>	+0.01°C / % feed rate	-3.2°C / % excess
<b>(D/F)V</b>	-0.4°C / % feed rate	+0.50°C / % excess

## 9.4 ONE-POINT CONTROL

### 9.4.1 Applicability of One-Point Control

One-point control schemes have been the backbone of industrial distillation control for many years, although the advent of multivariable predictive controllers (e.g. Dynamic Matrix Control, DMC) has recently seen a shift towards more complex strategies. However, one-point control is still widely practised and has some inherent advantages compared with open-loop and two-point control.

One-point control is relatively easy to implement, is not subject to interactions between opposing composition control loops and provides a form of effective constraint management. Distillation columns are almost always illconditioned due to the presence of high gain variables (e.g. external flows which change the material balance) and low gain variables (e.g. internal flows which change the energy balance). If a two-point control scheme is applied, the illconditioning can restrict the attainable closed-loop performance and, in extreme cases, create instability due to excessive interaction.

The ability to implicitly incorporate constraint management into a control scheme is often more important than the composition control of the secondary product in an industrial environment. This is possible with one-point control but is often difficult with two-point control as one less degree of freedom is present in the latter case. Throughput constraints such as column flooding and reboiler and condenser duty limitations are usually nearly proportional to the internal column flows. The manipulated variable that is not used for composition control in a one-point scheme can, therefore, be fixed at a value that corresponds closely to the equipment constraint. This is particularly effective if the unused manipulated variable is the reflux rate or reboiler duty as these variables substantially determine the internal column flows.

The relationship between the unused manipulated variable and the column constraints can also be seen if it is considered that the two degrees of freedom in a distillation process determine the feed-split and fractionation. In a two-point control scheme, the feed-split controls the primary product composition and fractionation control the secondary product composition. Fractionation is a function of the internal column flows, as are the likely column constraints (i.e. flooding, reboiler duty, etc.).

The properties of one-point distillation control make it an attractive option in many cases but, although only one composition control loop must be configured, the implementation of

a one-point control scheme for an ETBE column presents some difficulties. These aspects are discussed below and relate primarily to the selection of the controlled variable (Section 9.4.2) and the organisation of the manipulated variables (Section 9.4.3).

### 9.4.2 Control Objective

The controlled variable should always be selected in order to reflect the process objectives as reliably as possible. Before this can be done, it is necessary to determine the priority of the process objectives since there is only one available degree of freedom in a one-point control scheme. It is also necessary to find a means of determining whether the process objectives are being met.

The most important process objective is likely to be the control of the bottoms product composition as the process will normally be constrained by external quality specifications (e.g. minimum ETBE content, maximum Reid vapour pressure, etc.). This makes the bottoms product composition the most likely control objective. There are essentially three methods for monitoring product composition: (a) directly, with one or more online analysers; (b) indirectly, using a temperature or pressure corrected temperature to infer composition; and, (c) externally, using process samples taken at regular intervals and appropriate laboratory equipment. Analysers have many advantages but are costly, require regular maintenance and usually introduce a significant time delay into the process. Inferential control is cheaper and, often, more reliable but can also be less accurate. The use of external measuring equipment (e.g. laboratory techniques) limits the measurement frequency and is unsuitable for closed loop control.

If some form of inferential control is to be used (either in a closed-loop or open-loop system) to monitor product composition, the temperature sensor must be located carefully to ensure that changes in the composition are accurately reflected and good sensitivity to set point changes is provided. The reboiler sump is commonly used as a sensing location as it minimises process dead time and sensitivity is usually high (except with very high product purities). It might be expected that variations in the reboiler temperature (at constant pressure) would directly relate to changes in the product composition whereas other locations would be susceptible to interference from changes in the stage-to-stage composition profile. However, in an ETBE reactive distillation column, the relationship between reboiler temperature and bottoms composition is neither linear nor even monotonic, as indicated by Figure 9.1, which was produced from simulation data of the 10 stage ETBE column described previously. The absence of a one-to-one relationship prevents the reboiler temperature from being used to infer composition. The convex dependence will also lead to

controller instability as it is not clear from the measured temperature whether the reboiler duty (or bottoms rate) should be increased or decreased to change the ETBE purity towards its desired value.

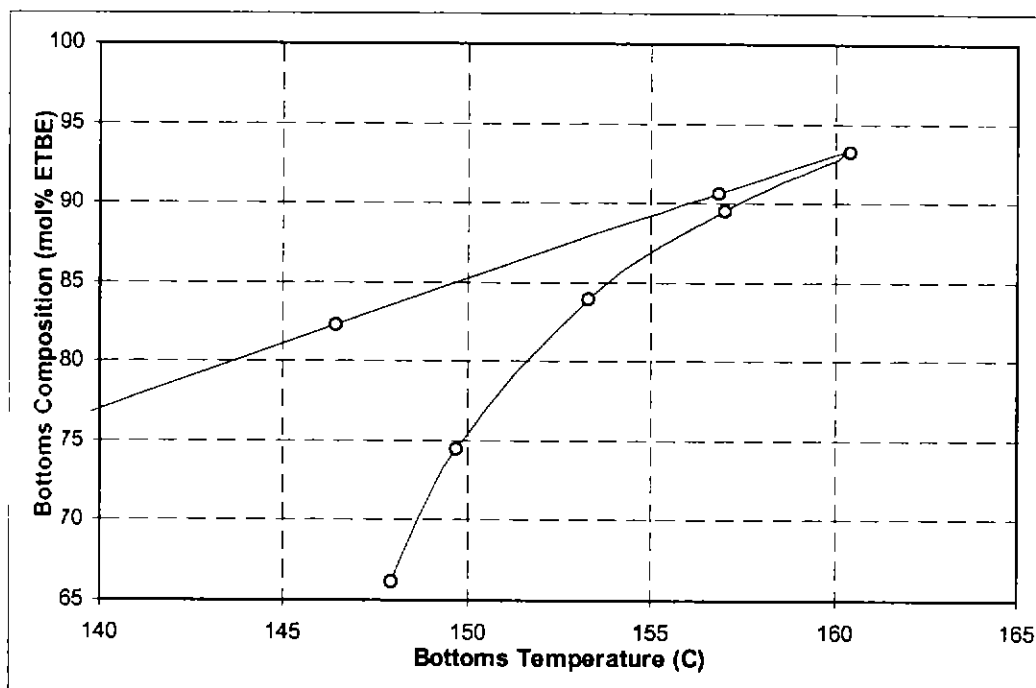
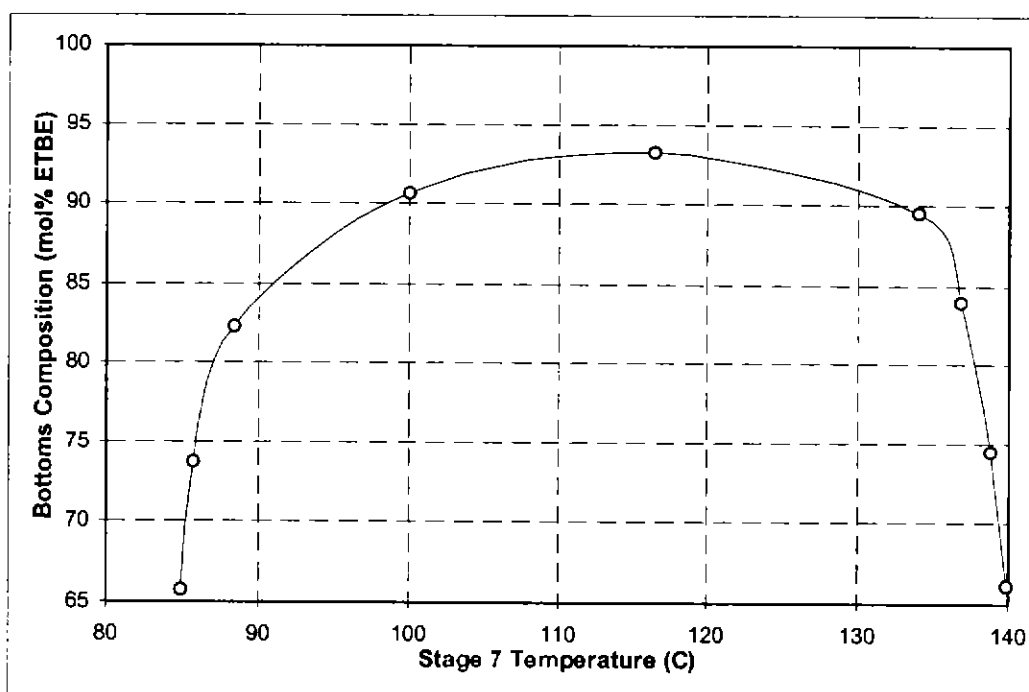


Figure 9.1 - Non-linear Relationship Between Bottoms Temperature and Composition

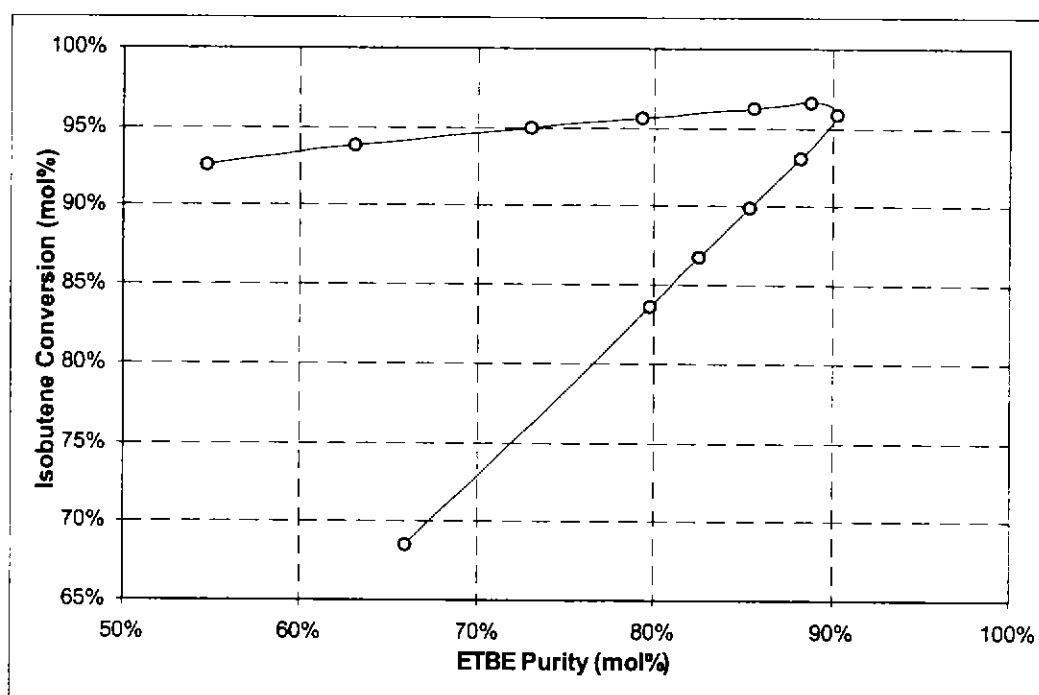
The best location for the temperature sensor in this column appears to be approximately midway between the feed point and the reboiler as that location provides adequate sensitivity and avoids any convex relationship with potential manipulated variables. Figure 9.2 shows how the liquid temperature on stage 7 (middle of the stripping section) relates to the bottoms composition and, although the relationship is still strongly non-linear, and a bottoms composition of, say 90 mol%, is obtained at two temperatures (approximately 99°C and 132°C), every temperature corresponds to one, and only one, composition. Therefore, the stripping section temperature uniquely defines the operating point of the column and is suitable for inferential control of the bottoms composition. The sensitivity is also high with a change of 5°C representing only a small change in ether purity near the optimum operating point. Shifting the sensing point away from the reboiler increases the dead time in the control loop but this cannot be avoided if a stable inferential controller is to be implemented.





**Figure 9.2 - Relationship Between Stripping Section Temperature and Bottoms Composition**

Alternatively, the isobutene conversion could be selected as the control objective. Direct measurement of the conversion would require complex, synchronised analysers on the feed, distillate and bottoms products plus a calculation module. This combination would clearly be difficult to implement successfully and prone to instrument uncertainty. It might also result in the production of unsaleable product since there would be no guarantee that the quality specifications would be observed. Fortunately, the coincidence of phase and chemical equilibrium is usually sufficiently large so that the reaction proceeds satisfactorily under most conditions. This is indicated in Figure 9.3, which predicts the isobutene conversion for a given ETBE purity in the bottoms product. Provided that a high purity is maintained, the conversion should remain acceptable too. Thus, it is better to control the bottoms composition directly rather than the isobutene conversion. Similar arguments apply to the other process objectives: provided that an appropriate purity target is selected and then maintained, the other process objectives will be mostly satisfied.



**Figure 9.3 - Relationship Between ETBE Purity and Isobutene Conversion**

The purity and conversion curves in Figure 9.3 do not correspond exactly and the maximum conversion is achieved at an ether purity just less than the maximum. The optimal operating point would probably be between the two maxima but would need to be determined for the specific column installation with respect to raw material costs and product values. Regular laboratory tests could be used to monitor the isobutene conversion and adjust the closed-loop control of the bottoms composition, as required, in a one-point control scheme.

Overall, it appears that a satisfactory one-point control scheme could be implemented using a temperature from the stripping section to infer the bottoms composition. This arrangement should allow the bottoms composition to be controlled between specification limits and the process to be managed around equipment constraints in order to maximise throughput. The secondary process objectives cannot be met directly as there are insufficient available degrees of freedom but the careful selection of operating point will allow satisfactory performance to be maintained.

#### 9.4.3 Control Configuration

The control configuration designations refer to the two manipulated variables that are not used for inventory control. In one-point control, one of these variables is used to control a product composition and one is fixed or adjusted only intermittently (normally to manage an equipment constraint). The distillate and bottoms product draw rates directly affect the feed split (i.e. the column material balance) while the reflux rate and reboiler duty only affect

fractionation. The relative magnitudes of these effects differ by approximately an order of magnitude so that the manipulated variable selected for composition control should be one of the product draw rates where a choice exists. With this restriction, it is possible to ascertain the variable pairings that are implied by each control configurations. These are indicated in Table 9.2 for several common control schemes, including some ratio schemes. Figure 9.4 depicts the control connections for the LV configuration. The other configurations can be setup similarly. The DB control structure is excluded because the two manipulated variables are not independent at steady state and, therefore, satisfactory one-point control is not realisable.

**Table 9.2 - Distillation Control Configurations**

<b>Configuration</b>	<b>Composition Control</b>		<b>Inventory Control</b>	
	<b>Varied</b>	<b>Fixed</b>	<b>Reflux Accumulator</b>	<b>Reboiler Sump</b>
LV	reflux rate or reboiler duty	reboiler duty or reflux rate	distillate rate	bottoms rate
LB	bottoms rate	reflux rate	distillate rate	reboiler duty
DV	distillate rate	reboiler duty	reflux rate	bottoms rate
(L/D)V	reboiler duty	reflux ratio	distillate rate	bottoms rate
(L/D)(V/B)	reflux ratio or boilup ratio	boilup ratio or reflux ratio	distillate rate	bottoms rate
(V/B)L	reflux rate	boilup ratio	distillate rate	bottoms rate
(D/F)V	distillate yield	reboiler duty	reflux rate	bottoms rate

Some general process control rules can expedite the selection of the best control structure for a particular column. Firstly, the control scheme should combine steady state sensitivity and dynamic responsiveness (Neisenfeld and Seeman, 1981). Since the sensing point for the 10 stage ETBE column that is examined here has been specified to be near the middle of the stripping section, the reboiler duty (V) and bottoms draw rate (B) are favoured as the principal manipulated variables although other choices might also show a good sensitivity for the controlled variable. Secondly, the level control is favoured by the use of the larger outlet stream when more than one exists from a given vessel (Luyben, 1992). This implies using reflux rate to control the reflux accumulator level on columns where the reflux ratio is higher than unity and the reflux rate when the converse applies. This consideration favours the DV configuration for columns with high reflux ratio and the LV, LB and ratio configurations for columns with low reflux ratio.

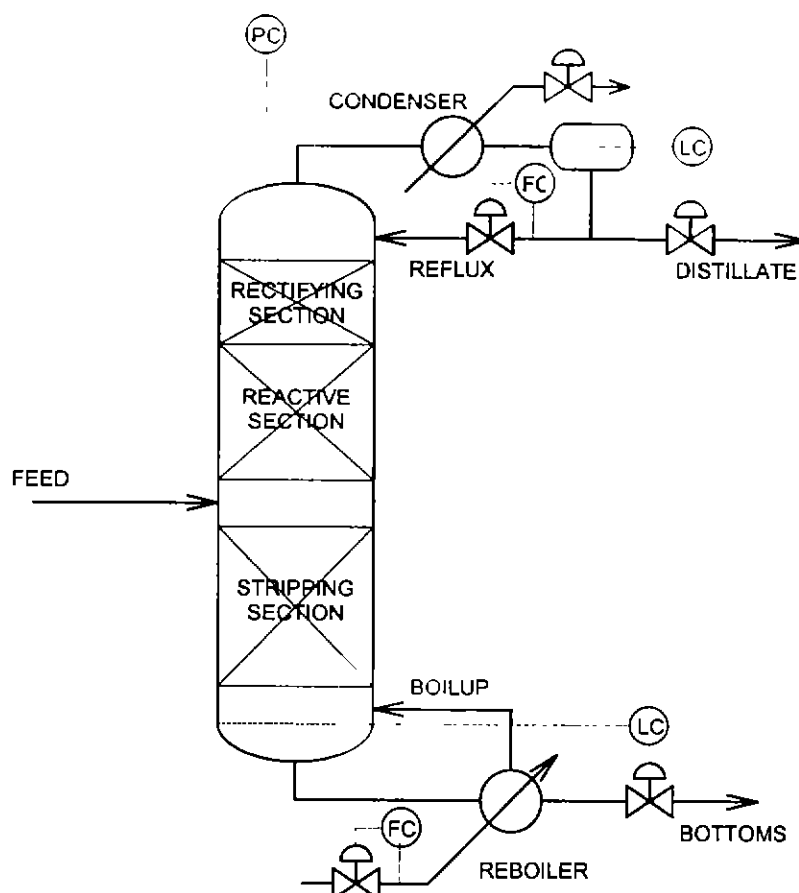


Figure 9.4 - LV Control Configuration

The ratio control schemes have been strongly recommended by some authors (e.g. Skogestad and Morari, 1987; Shinskey, 1984) but are generally more suited to two-point control. These schemes effectively result in one or more non-diagonal 2x2 controllers (i.e. a MIMO controller instead of several SISO controllers). For example, schemes involving  $L/D$  or the reflux ratio  $L/(L+D)$  lead to a controller that manipulates both  $L$  and  $D$  for reflux drum level control, regardless of how the composition ratio is configured. The advantages of ratio control schemes generally centre on the implicit decoupling that is achieved (Sandelin et al., 1991). For example, the reflux ratio and boilup ratio are essentially independent while the reflux rate and the reboiler duty are closely related. This feature of ratio control schemes is highly advantageous for two-point composition control but less important for one point composition control where control loop interactions are less significant. The disadvantages of ratio schemes are that they often make consistent operation at equipment constraints harder to achieve and they increase the complexity of the control problem.

No clear preference for any control configuration is evident for the 10 stage ETBE column. However, dynamic simulation provides a means of quickly assessing each scheme. Perfect

level and pressure control was assumed and a simple PI controller was implemented in the simulation to control the liquid temperature on stage 7 (middle of the stripping section). The tuning constants were determined empirically to approximately produce quarter decay responses. The attainable control performance was tested against two common disturbances (a feed rate step increase of 8% and a feed composition step increase of 2% to the ratio of ethanol to isobutene) and a set point change of 5°C. The results are presented in Figures 9.5-9.13 and summarised in Table 9.3 in terms of the integrated absolute error (IAE) and the integrated time-weighted absolute error (ITAE) of the controlled variable.

**Table 9.3 - Control Scheme Performance**

Scheme	Feed Rate Step Increase (+8%)		Feed Composition Step Increase (+2%)		Set Point Change (+5°C)	
	IAE	ITAE	IAE	ITAE	IAE	ITAE
LV	0.3	0.6	0.05	0.3	1.3	2.2
LB	0.4	0.8	0.05	0.1	0.6	1.0
DV	42	430	1.4	7.8	15	73
(L/D)V	0.8	2.3	0.07	0.6	1.6	3.4
(L/D)(V/B)	0.1	0.6	0.1	0.6	1.5	2.5
(D/F)V	11	400	0.1	0.7	1.5	2.5

If only the basic (non-ratio) control structures are considered, Table 9.3 suggests that either the LV or the LB configuration is most suitable but this is less evident from the simulation responses shown in Figures 9.5-9.13. The LV (Figures 9.5-9.7) and LB (Figures 9.8-9.10) configurations produced a faster response to a feed rate change than the DV scheme (Figures 9.11-9.13) and the deviation from the initial conditions was less. The latter point is significant since the product composition is not being measured or controlled directly. However, the dynamic responses of the ether product to changes in the feed composition and set point appeared similar for all configurations, despite the much higher IAE and ITAE for the DV configuration.

These initial results suggest that the presence of a reaction (or a reactive section) within the column has a significant effect on the performance of the control system. The DV configuration is very widely used in industry for conventional distillation columns, including those where the primary product is the column bottoms, and normally yields very satisfactory results based on controlling the feed split. However, in this reactive distillation column, manipulating the feed split does not necessarily ensure that satisfactory reaction

conditions are maintained and a control configuration that manipulates the reboiler energy input (either directly with the LV configuration or indirectly with the LB configuration) is preferred.

The performances of the ratio schemes were varied, and usually slightly inferior to the LV and LB configurations, but the double ratio configuration appears to have potential. The dynamic simulation responses are similar to those shown in Figures 9.5-9.13 but have not been included here due to space limitations. These results provide no clear incentive to install a ratio scheme on this column and, given the increased complexity and the disadvantages discussed previously, a non-ratio scheme should be implemented in this column.

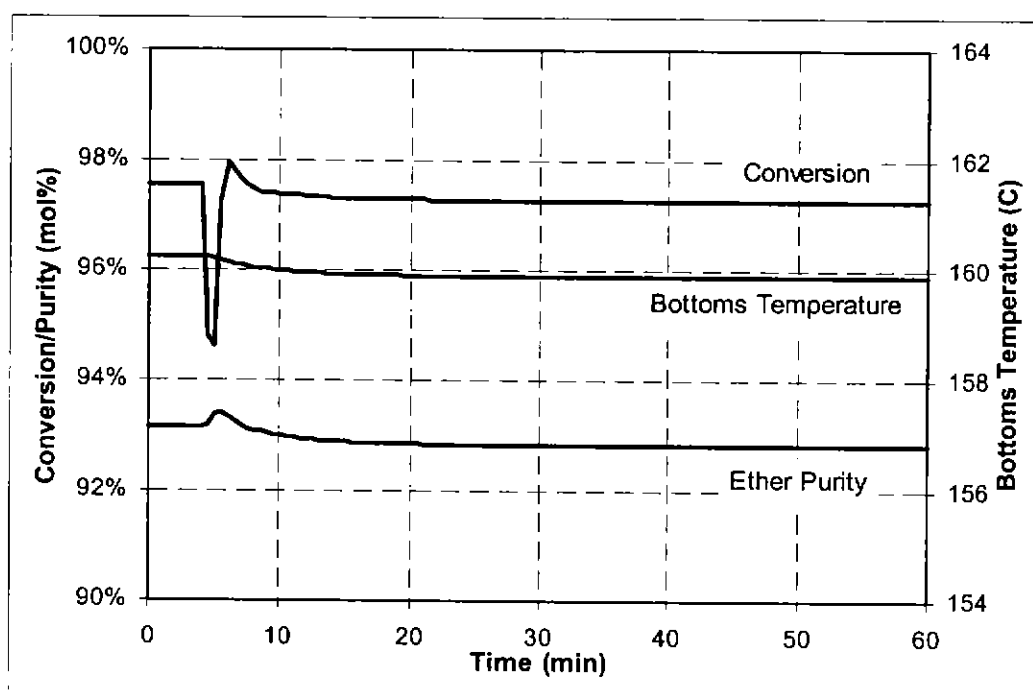


Figure 9.5 - Step Increase in Feed with the LV Configuration

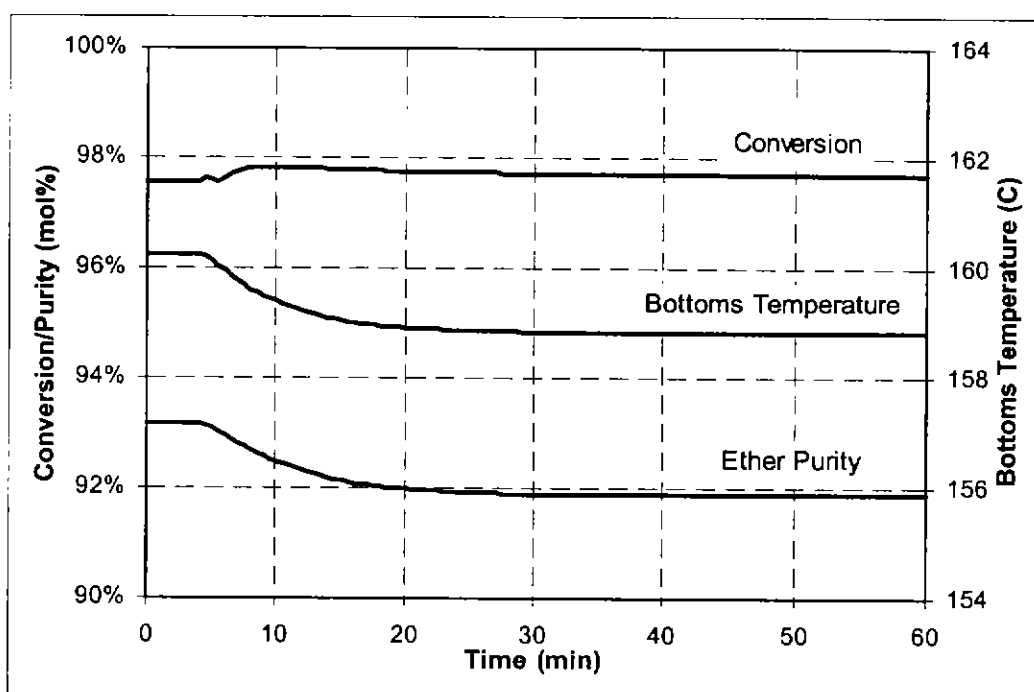


Figure 9.6 - Step Change in Feed Composition with the LV Configuration

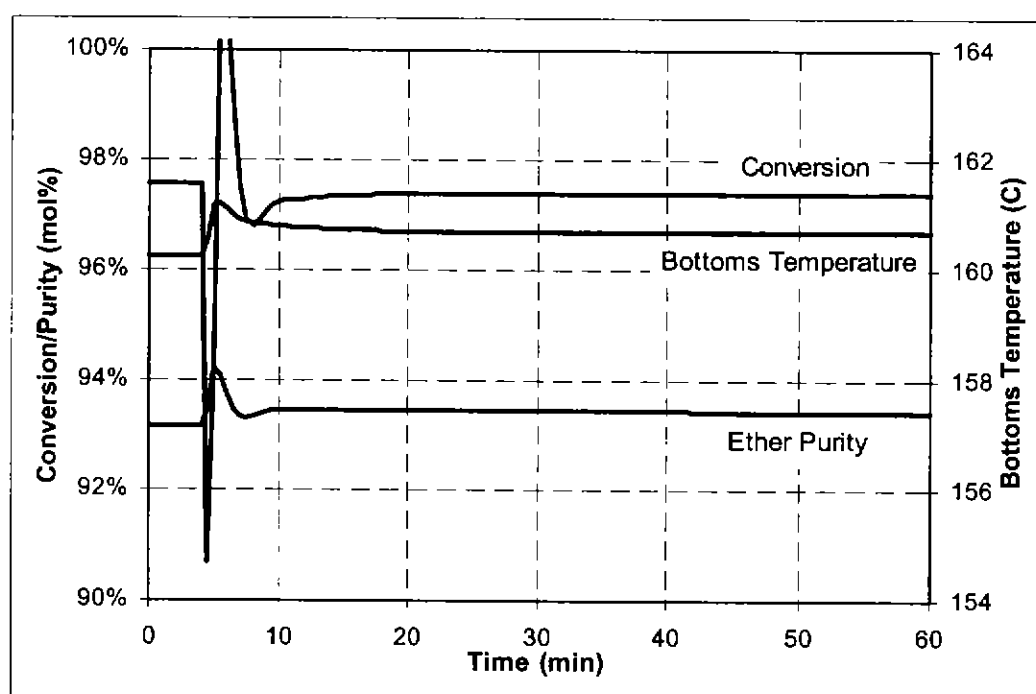


Figure 9.7 - Step Change in Set Point with the LV Configuration

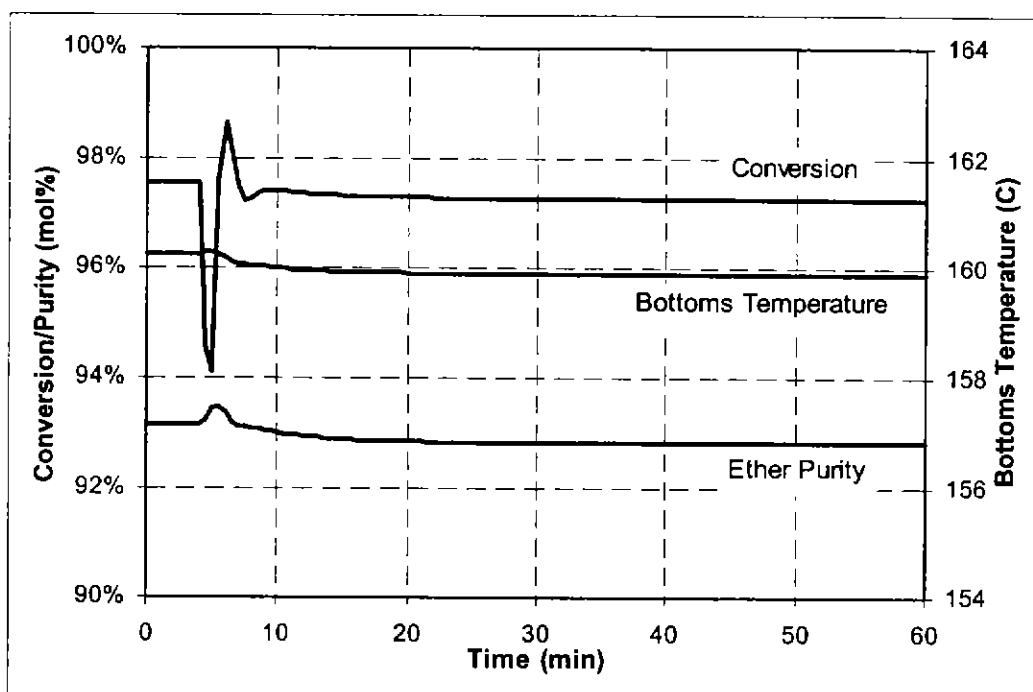


Figure 9.8 - Step Increase in Feed with the LB Configuration

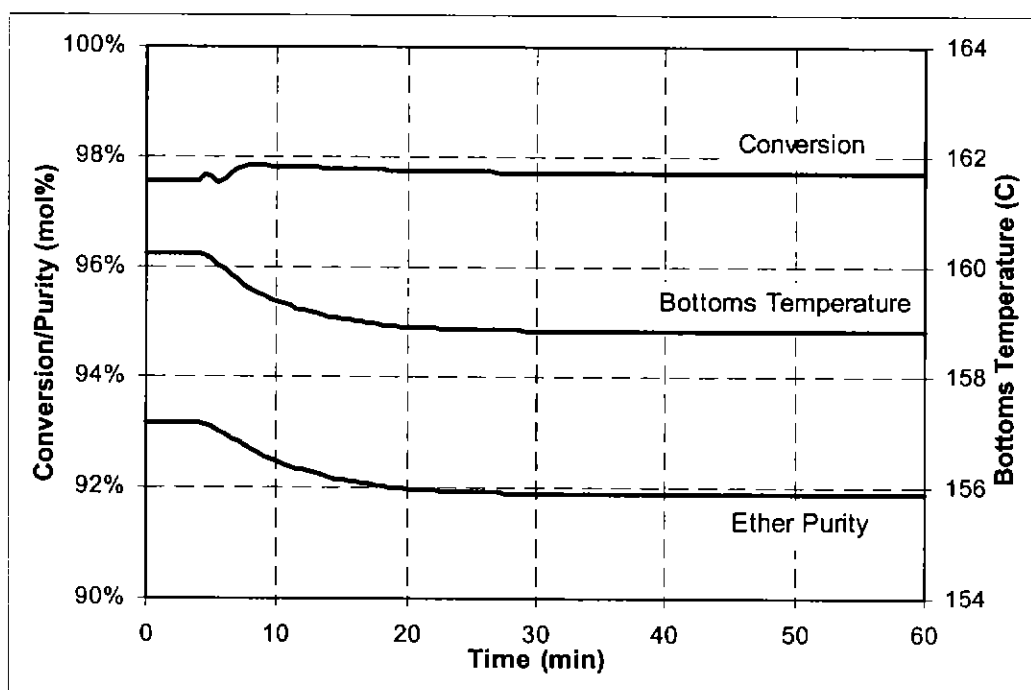


Figure 9.9 - Step Change in Feed Composition with the LB Configuration



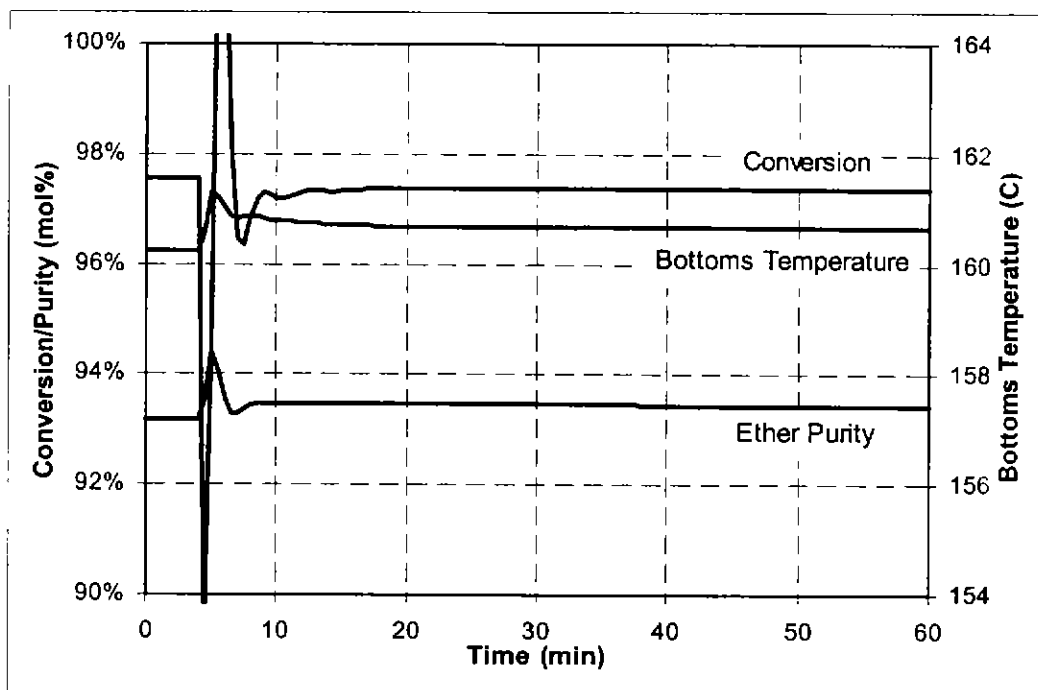


Figure 9.10 - Step Change in Set Point with the LB Configuration

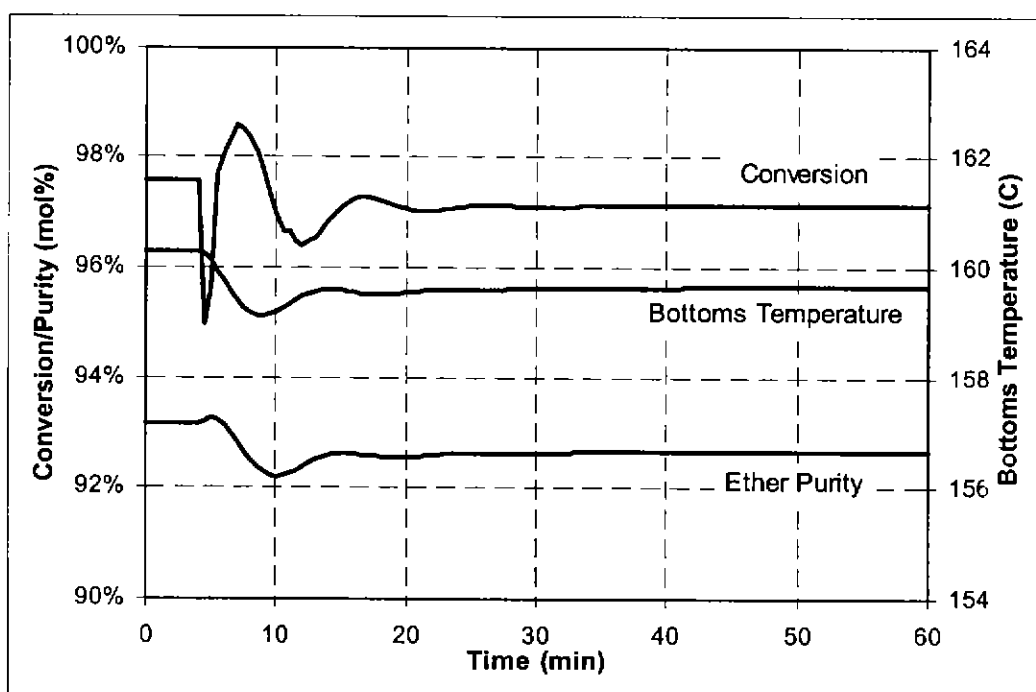


Figure 9.11 - Step Increase in Feed with the DV Configuration

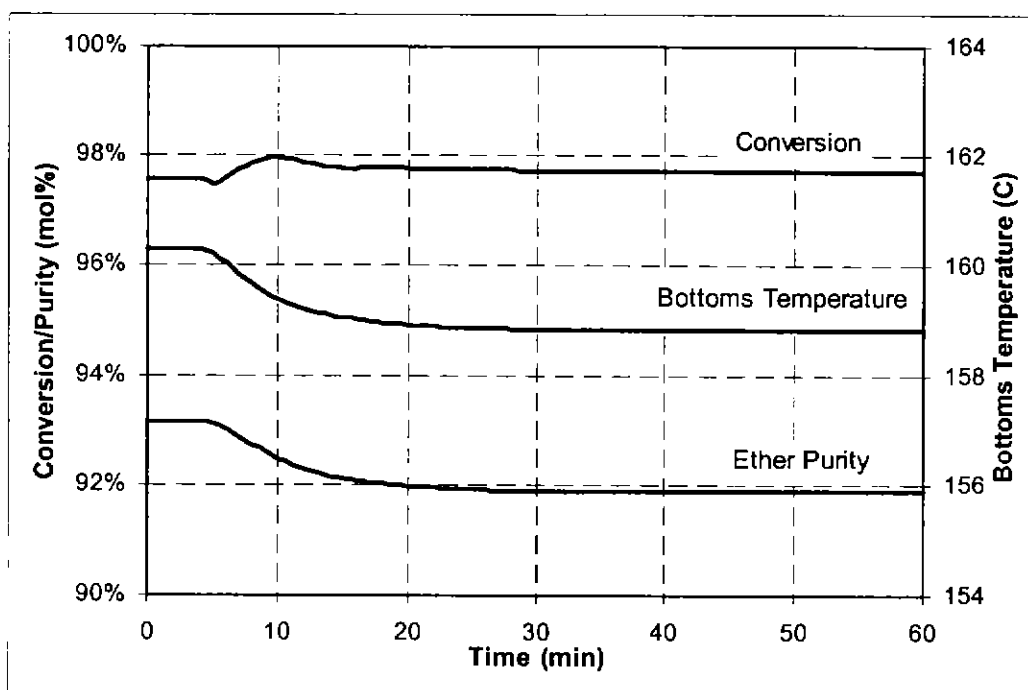


Figure 9.12 - Step Change in Feed Composition with the DV Configuration

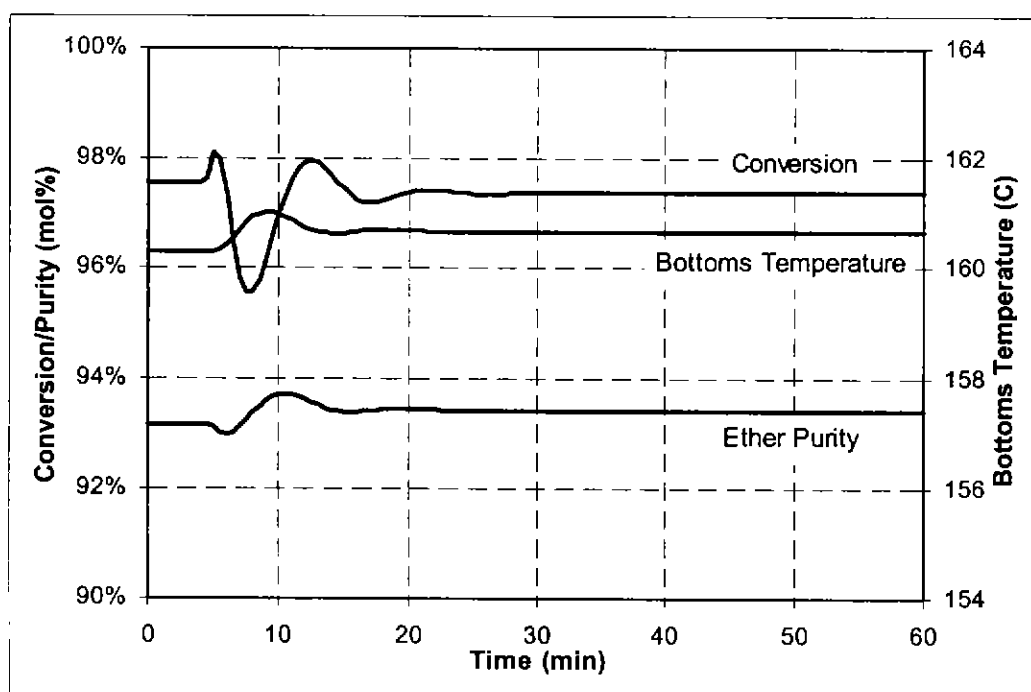


Figure 9.13 - Step Change in Set Point with the DV Configuration

A final comparison can be made between the various control structures: the ability of each configuration to support operation at an equipment constraint. This can be investigated by considering the magnitude of the control moves required to counteract feed rate and composition disturbances and a set-point change. These values were calculated from dynamic simulation results and have been tabulated in Table 9.4. The  $\Delta$  denotes the change in either the reboiler duty or the reflux rate due to the change in set-point. A small value indicates that operation can continue close to the equipment constraint while a larger value indicates that the operation become infeasible (i.e. exceeds an equipment constraint) or results in under-utilisation of the available resources. Clearly, the LV and the LB configurations perform best in this regard.

**Table 9 4 - Departure from Equipment Constraints**

Scheme	Feed Rate Step Increase (+8%)		Feed Composition Step Increase (+2%)		Set Point Change (+5°C)	
	$\Delta Q_R$	$\Delta L$	$\Delta Q_R$	$\Delta L$	$\Delta Q_R$	$\Delta L$
LV	+2.6%	0	0	0	+0.2%	0
LB	+2.6%	0	0	0	+0.2%	0
DV	0	-4.0%	0	-0.07%	0	-0.4%
(L/D)V	+8.2%	+8.1%	0	-0.08%	+0.6%	+0.4%
(L/D)(V/B)	+8.2%	+8.1%	0	-0.08%	+0.6%	+0.4%
(D/F)V	+8.3%	+8.2%	-2.8%	-4.6%	+13.6%	+20.4%

Overall, there is little distinction between the LV and the LB control structures. Both provide good dynamic responsiveness and the ability to consistently operate close to equipment constraints and the results of the dynamic simulations suggest that either of these could be used effectively for one-point control of the 10 stage reactive ETBE column described in Chapter 3.

## CHAPTER TEN

### CONTROL ISSUES II - ADVANCED CONTROL

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  - 10.1.2 Inferential Conversion Model
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  - 10.3.1 Changing Process Objectives
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  - 10.3.3 Operating Modes of the Integrated Controller
    - 10.3.3.1 Control Mode 1*
    - 10.3.3.2 Control Mode 2*
    - 10.3.3.3 Control Mode 3*
  - 10.3.4 Controller Performance Tests
  - 10.3.5 Effectiveness of the Integrated Control Scheme
- 10.4 Overall Summary of Findings on Process Dynamics and Control Issues**

### 10.1 TWO-POINT CONTROL

#### 10.1.1 Process Objectives (Revisited)

It was noted in Chapter 9 that there are usually at least two major process objectives in reactive distillation: to control the purity of the desired product; and to maximise the conversion of reactants. Only one of these objectives can be satisfied automatically with a one-point control structure although some implicit control of the secondary objective might be realisable if the control system is formulated well. If more direct and exact control of the secondary objective is required, two-point control must be implemented. A third process objective (e.g. the degree of separation of key components, the ETBE or ethanol purity in

the distillate or sustained operation at an equipment constraint) cannot be achieved due to insufficient degrees of freedom.

Clearly, there are several combinations of process objectives that could be given priority. One-point control was shown to be effective when the product purity and throughput were considered to be most important. A conventional two-point distillation controller could be implemented when the ETBE or ethanol concentration in the distillate was the preferred secondary point of control. This is equivalent to controlling the separation or fractionation provided by the column and is incompatible with effective constraint management. However, the desire to simultaneously control a product purity and a reactant conversion is specific to reactive distillation and a standard approach is not available. This combination is considered here and implemented (via dynamic simulation) on the 10 stage ETBE column.

The use of a stripping section temperature to infer the bottoms composition was demonstrated in Chapter 9. The control configuration that was established with this measurement (using the reboiler duty) was also demonstrated and requires no modification for two-point control. However, a second control loop must now be configured to provide control of the reactant conversion. This requires the selection of appropriate controlled and manipulated variables. It was noted in Chapter 9 that the direct measurement of the isobutene conversion was unrealistic because it required synchronous results from at least three process analysers. Therefore, some form of inferential measurement is required.

## **10.1.2 Inferential Conversion Model**

### *10.1.2.1 Model Basis*

One of the advantages of the one-point control scheme was that it provided some implicit control of the isobutene conversion. This was achieved via the control of a temperature within in the stripping section, which effectively governed the entire temperature profile. A favourable composition was maintained on the stages just below the reactive section by preventing the temperature from becoming too high (a condition that corresponds to a deficiency of isobutene) or too low (corresponding to a deficiency of ethanol). Thus, the temperatures in the reactive and stripping sections might provide a means of inferring the isobutene conversion. Unfortunately, no single measurable variable correlates adequately with conversion.

This result is, perhaps, not surprising given the complexity of the system and the range of competing influences on the reaction zone conditions. For example, a decreased reaction zone temperature has a favourable effect on the reaction equilibrium constant but reduces

the reaction rate constant. It also indicates a greater availability of isobutene, which promotes the reaction (ethanol has a retarding effect on the reaction rate: Jensen and Datta, 1995), and a higher concentration of non-reactive butenes, which reduces the maximum conversion due to dilution effects. This suggests that any conversion prediction method should reflect the values of at least two (and possibly more) independent variables.

Two approaches to the development of an inferential conversion model appear promising. Firstly, the reactive distillation system could be represented by a simplified model (e.g. using short-cut methods to calculate the feed split and fractionation under given input conditions) to predict the column behaviour to measured disturbances. These results could then be used to calculate the expected conversion. However, no such short-cut methods are available for reactive distillation and the known complexity of the process is contrary to the applicability of such a model.

The second approach is to utilise the statistical analysis of a quantity of data that contains a range of measurable variables and the dependent variable (i.e. the isobutene conversion). The data could either be from actual operation of the process or generated by simulations. In this case, simulation data was used. This eliminates process noise and measurement uncertainty from the inferential model but results in the inclusion of model uncertainty. It is desirable to base the model on sound engineering principles but regression analysis can be an invaluable tool in developing a suitable model that is both effective and robust. The statistical approach was applied here to develop an inferential model for the ETBE column. The actual implementation of any such model requires process noise to be filtered in order to be effective. However, tools are readily available for this end, and the requirement for an on-line filter is not a barrier to this approach.

The first stage of this process was the selection of candidate variables that would appropriately reflect the reaction environment and the column operating conditions. The ease of measurement (both the cost and the probable accuracy) was considered important, and temperatures and flows were preferred on that basis. Composite variables were also considered to incorporate possible non-linear behaviour. A greater representation of stripping section temperatures was specified to reflect the larger temperature differences and the greater sensitivity to operating conditions compared with the reactive and the rectifying sections. The full list of candidate variables is given in Table 10.1.

Table 10.1 - Candidate Variables for Inferential Conversion Model

Variable Name	Description
$x_1$	Condenser temperature
$x_2$	Temperature at the top of the reaction zone (stage 3)
$x_3$	Temperature at the bottom of the reaction zone (stage 5)
$x_4$	Stage 7 temperature
$x_5$	Stage 8 temperature
$x_6$	Stage 9 temperature
$x_7$	Reboiler temperature
$x_8$	Reflux rate
$x_9$	Reboiler duty
$x_{10}$	Bottoms rate (yield)
$x_{11}$	Overhead pressure
$x_{12}$	Bottoms composition (via a process analyser)
$x_{13}$	$\Delta T$ across the reaction zone

Model identification can be achieved using either simulation data or real plant data. Simulation data will contain modelling errors but will be free of instrument errors and noise that may be present in plant data. The choice of data source (simulation or plant data) should be made on a case-by-case basis but if a good model of the process exists, the collection of data that spans the entire significant operating range can be achieved more efficiently using a simulation. The use of a simulation was preferred here although some experimental data was also available. The significant operating range was taken to include reboiler duties of 7.3-9.3 kW, reflux rates of 2.0-3.0 L/min and stoichiometric excesses of ethanol in the feed of 0-10%. A constant overhead pressure was assumed here but if significant perturbations in pressure were expected it could be added to the analysis. The data could have been generated using a factorial experimental design but since there was essentially no cost involved in the data generation, a less rigorous approach was used. The three primary variables (reboiler duty, reflux rate and ethanol excess) were each incremented around the optimum operating point to produce 25 observations which effectively spanned the significant operating range.

### 10.1.2.2 Two-Term Regression Models

Initially, two-term models were considered using various combinations of the candidate variables listed in Table 10.1. Some of the more promising combinations of variables are summarised in Table 10.2 with calculated regression coefficients ( $R^2$ ). Variables were judged to be statistically significant at the 95% confidence level.

**Table 10.2 - Candidate Two-Term Regression Models**

<b>Model Designation</b>	<b>Variables in Model</b>	<b><math>R^2</math></b>	<b>Standard Error of the Prediction</b>	<b>Statistically Significant Variables</b>
2 <sup>A</sup>	$x_1$ & $x_2$	0.996	0.6 mol%	$x_1$ & $x_2$
2 <sup>B</sup>	$x_1$ & $x_3$	0.970	1.8 mol%	$x_1$ & $x_3$
2 <sup>C</sup>	$x_1$ & $x_7$	0.976	1.6 mol%	$x_1$ & $x_7$
2 <sup>D</sup>	$x_2$ & $x_3$	0.898	3.3 mol%	$x_2$ only
2 <sup>E</sup>	$x_2$ & $x_4$	0.965	1.9 mol%	$x_2$ & $x_4$
2 <sup>F</sup>	$x_2$ & $x_5$	0.985	1.3 mol%	$x_2$ & $x_5$
2 <sup>G</sup>	$x_2$ & $x_6$	0.990	1.0 mol%	$x_2$ & $x_6$
2 <sup>H</sup>	$x_2$ & $x_7$	0.986	1.2 mol%	$x_2$ & $x_7$
2 <sup>I</sup>	$x_2$ & $x_8$	0.900	3.3 mol%	$x_2$ only
2 <sup>J</sup>	$x_2$ & $x_9$	0.915	3.0 mol%	$x_2$ only
2 <sup>K</sup>	$x_2$ & $x_{10}$	0.952	2.3 mol%	$x_2$ & $x_{10}$
2 <sup>L</sup>	$x_2$ & $x_{12}$	0.982	1.4 mol%	$x_2$ & $x_{12}$
2 <sup>M</sup>	$x_3$ & $x_7$	0.888	3.5 mol%	$x_3$ & $x_7$
2 <sup>N</sup>	$x_4$ & $x_8$	0.427	7.8 mol%	$x_4$ only
2 <sup>O</sup>	$x_{10}$ & $x_{11}$	0.674	5.9 mol%	$x_{11}$ only

The best model (2<sup>A</sup>) was rejected because of sensitivity between the condenser temperature and the conversion estimate. The calculated regression coefficient was 18.7 which indicates that a 1°C change in the condenser temperature (for whatever reason) would change the conversion estimate by 18.7 mol%. This level of sensitivity is too high and would significantly reduce the robustness of the model to instrument error and/or modelling errors. Similarly, other models which included  $x_1$  as a manipulated variable were also excluded as the calculated regression coefficient for  $x_1$  was usually greater than 10.

Three models (2<sup>F</sup>, 2<sup>G</sup> and 2<sup>H</sup>) were found to have a  $R^2$  value greater than 0.98, which is highly acceptable. Interestingly, the model which uses the bottoms composition directly



(model 2<sup>L</sup>), is not as good as models 2<sup>F</sup>, 2<sup>G</sup> or 2<sup>H</sup>, although the differences are small. The vector forms of each of these models are given by equations (10.1)-(10.3), where  $y$  is the conversion estimate:

$$y = \begin{bmatrix} -4.187 & 0.169 \end{bmatrix} \begin{bmatrix} x_2 \\ x_5 \end{bmatrix} + 409.1 \quad (10.1)$$

$$y = \begin{bmatrix} -3.889 & 0.161 \end{bmatrix} \begin{bmatrix} x_2 \\ x_6 \end{bmatrix} + 384.3 \quad (10.2)$$

$$y = \begin{bmatrix} -3.534 & 0.187 \end{bmatrix} \begin{bmatrix} x_2 \\ x_7 \end{bmatrix} + 349.5 \quad (10.3)$$

The constants in each model have similar values that suggest an underlying relationship between the reaction zone and the stripping zone temperatures, and the isobutene conversion. A temperature increase of 1°C at the top of the reaction zone (stage 3) should decrease conversion by 3-4 mol% while an increase of 1°C in temperatures near the bottom of the column should increase the conversion by 0.15-0.20 mol%. Using model 2<sup>G</sup> as an example, the engineering significance of the terms is possibly that a higher reaction zone temperature implies a decreased availability of isobutene and a less favourable reaction equilibrium constant while an increase in the stage 9 temperature implies a higher reaction rate as ETBE is the highest boiling point component.

Interestingly, the temperature at the top of the reaction zone (stage 3) shows a much stronger correlation with the conversion than the temperature at the bottom of the reaction zone (stage 5) which shows a much greater variation. This can be explained with reference to the ethanol concentration in the distillate product. A high ethanol concentration would increase the VLE temperature on the uppermost stages in the column and also indicates a low isobutene conversion as the reaction is equimolar in isobutene and ethanol. Conversely, a low ethanol concentration would result in low temperatures on the uppermost stages and would indicate a high conversion of ethanol (and isobutene).

Fortunately, the best two-term models exclude manipulated variables ( $x_8$ ,  $x_9$  and  $x_{10}$ ). This is convenient as it simplifies the implementation of a closed-loop inferential controller. If a manipulated variable had been included in the model, there would be potential for a feedback loop to form. The inferential controller would have had a tendency to drive that variable to 0% or 100% of range (depending on whether the variable had a positive or negative effect on the conversion).

### 10.1.2.3 Three-Term Regression Models

The correlation coefficient of model 2<sup>G</sup> is already high but could possibly be increased further by including additional terms in the model. Several three-term models were evaluated and have been summarised in Table 10.3. None of these models are significantly better than the two-term models, 2<sup>F</sup>, 2<sup>G</sup> and 2<sup>H</sup>. Therefore, there is no incentive to further complicate the model by adding extra terms. A check of the residuals also shows that none of the available independent variables should be added to the model as the relationships between these variables and the residuals is essentially random in all cases.

**Table 10.3 - Candidate Three-Term Regression Models**

<b>Model Designation</b>	<b>Variables in Model</b>	<b>R<sup>2</sup></b>	<b>Standard Error of the Prediction</b>	<b>Statistically Significant Variables</b>
3 <sup>A</sup>	x <sub>2</sub> , x <sub>6</sub> , x <sub>8</sub>	0.992	0.9 mol%	all
3 <sup>B</sup>	x <sub>2</sub> , x <sub>6</sub> , x <sub>10</sub>	0.990	1.0 mol%	x <sub>2</sub> & x <sub>6</sub> only
3 <sup>C</sup>	x <sub>2</sub> , x <sub>6</sub> , x <sub>11</sub>	0.990	1.0 mol%	x <sub>2</sub> & x <sub>6</sub> only
3 <sup>D</sup>	x <sub>2</sub> , x <sub>7</sub> , x <sub>8</sub>	0.987	1.2 mol%	x <sub>2</sub> & x <sub>7</sub> only
3 <sup>E</sup>	x <sub>2</sub> , x <sub>3</sub> , x <sub>6</sub>	0.990	1.0 mol%	x <sub>2</sub> & x <sub>6</sub> only
3 <sup>F</sup>	x <sub>2</sub> , x <sub>5</sub> , x <sub>7</sub>	0.990	1.0 mol%	all
3 <sup>G</sup>	x <sub>3</sub> , x <sub>4</sub> , x <sub>7</sub>	0.945	2.5 mol%	x <sub>3</sub> & x <sub>4</sub> only

There is insufficient justification for differentiating between models 2<sup>F</sup>, 2<sup>G</sup> and 2<sup>H</sup> with respect to the statistical fit but model 2<sup>H</sup> might be preferred to minimise equipment costs as it is likely that the reboiler temperature will already be measured for other reasons. Furthermore, model 2<sup>H</sup> shows the least sensitivity to the reaction zone temperature and this might contribute to the model's robustness. This model is sufficiently accurate to be used for closed-loop control and is simple enough to implement easily and to operate robustly.

This model is independent of pressure and would be suitable for a system where the pressure was tightly controlled and not susceptible to significant disturbances. If pressure fluctuations were anticipated to have a significant effect on the column operation two options exist for modifying the model. Firstly, the temperature measurements could be corrected for pressure using known VLE relationships. This is common in many operating facilities. Secondly, a new inferential model could be built using simulation data generated over the relevant pressure range. This type of model should be able to reflect the effect of pressure on temperature and also the effect pressure has on the overall column performance

(including its direct impact on the reaction via changes in the reaction equilibrium constant and the stage-to-stage compositions), and might, therefore, be preferred.

There is clear potential to significantly improve the operation of ETBE reactive distillation columns through the use of inferential conversion models that could be applied to the simultaneous control of the isobutene conversion and the ether product purity. Separation considerations often predominate in the reactive distillation of MTBE, as the reaction can be expected to proceed at an acceptable rate over a wide range of conditions, but an inferential conversion model would be equally applicable and could be implemented with similar advantages. As well as the potential for closed-loop control, the additional process information that would be provided from a conversion prediction model would be highly valuable for routine process optimisation. An inferential model could also be developed for MTBE systems using the techniques demonstrated here.

### 10.1.3 Combined Composition and Conversion Control

The operation of reactive distillation processes requires careful optimisation: increasing the product purity too far (by manipulating the reboiler duty or by some other means) can significantly inhibit the reaction. Satisfactory operation is certainly possible with a one-point (composition only) control scheme but satisfying the primary operating objective (e.g. the bottoms purity specification) does not necessarily guarantee adequate process performance. A very low reactant conversion can still result from operating conditions that satisfy the purity requirement, and effective control of the reaction should be considered vital.

A combined composition and conversion control scheme which automatically ensures that satisfactory reaction conditions are maintained was implemented on the ETBE column using the inferential conversion model described in Section 10.1.2 and the LV control configuration. The five degrees of freedom that are available are utilised according to the variable pairings given in Table 10.4. The reboiler duty and reflux rate were assigned for composition and conversion control, respectively. The distillate draw rate and bottoms draw rate were assigned to level control according to dynamic responsiveness considerations and the condenser duty was used for pressure control as is the popular convention. This arrangement is also shown diagrammatically, Figure 10.1, to indicate where the inferential model was applied. An alternative control structure could have been developed using the bottoms draw rate for composition control and the reflux rate for conversion control: similar results would have been achieved. However, transposed couplings (reflux rate to control

composition and reboiler duty or bottoms rate to control conversion) would yield poor dynamic responsiveness and is not recommended.

Table 10.4 - Variable Pairings for Two-Point Reactive Distillation Control.

Controlled Variable	Manipulated Variable
Pressure (overhead)	Condenser duty
Reflux accumulator level	Distillate draw rate
Reboiler sump level	Bottoms draw rate
Bottoms composition (ether purity)	Reboiler duty
Isobutene conversion	Reflux rate

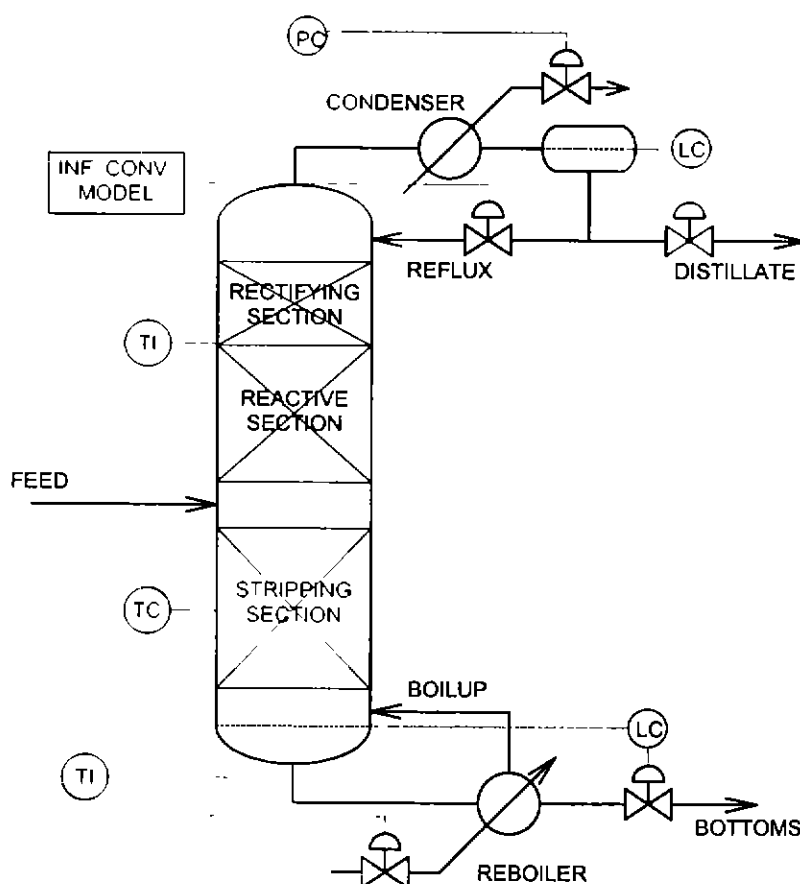
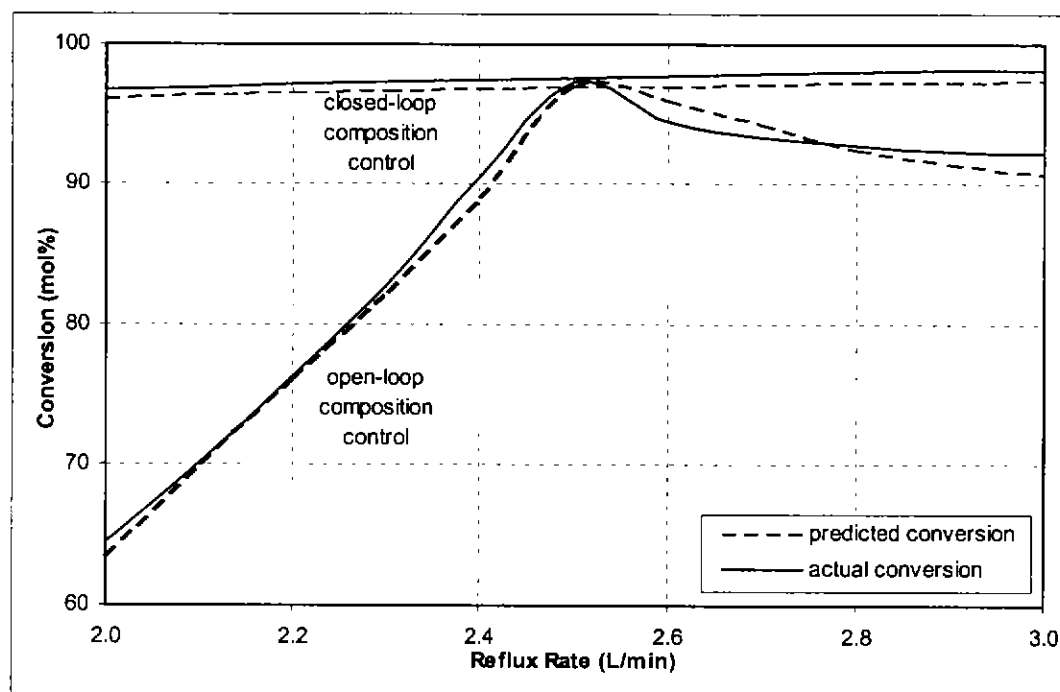


Figure 10.1 - Two-Point Control Configuration for ETBE Reactive Distillation Column

The considerations of linearity, sensitivity and responsiveness apply to the implementation of the inferential conversion model equally as they did to the composition controller. Figure 10.2 shows the relationship between the actual isobutene conversion (as determined from the full simulation model) and the predicted conversion (determined from the inferential model), and the reflux rate. When the composition control is operated in open-loop (constant reboiler duty), both the actual conversion and the inferential model are highly non-

linear and non-monotonic with respect to the reflux rate, making it unsuitable for use in a closed-loop control system. However, if the composition controller is operated in closed-loop, both the actual conversion and the inferential model are monotonic increasing and close to linear over the entire operating range. Therefore, as part of a two-point control scheme, the inferential model has good characteristics.



**Figure 10.2 - Linearity of the Inferential Conversion Model**

Sensitivity was considered in the development of the inferential model and in the selection of the preferred model but Figure 10.2 indicates only a low sensitivity between the reflux rate and the predicted conversion (in closed-loop mode). This is primarily a result of the implicit conversion control produced by the composition controller. An uncertainty of only  $0.2^{\circ}\text{C}$  in both of the temperature measurements equates to a maximum error of  $0.7\text{ mol}\%$  in the predicted conversion. While this is significant (it could result in a 20% change in the reflux rate), high sensitivity is inherent in the process (as with other high-purity distillation processes), and several techniques, including time series averaging or variable filtering, could be used to overcome any erratic tendency in the model output. The greatest contribution to the conversion prediction is from the temperature at the top of the reactive section (stage 3) so that dynamic responsiveness should be good. Overall, the inferential model appears to be suitable for closed-loop operation.

Controller performance is always a strong function of the tuning parameters and it is difficult to compare alternative control schemes on an even basis. Two options exist: tune

both (all) schemes using a single criteria (e.g. singular value decomposition, SVD) or a particular set of tuning rules (e.g. the Ziegler-Nichols constants); or compare perfect controller performance (i.e. controlled variables always at set-point) for both configurations. The reactive distillation process is inherently complex and cannot be adequately represented with simple linear models. Bode plots can be produced using a dynamic simulation model but the results are inconclusive due to the presence of higher-order lags and dead-times. Other tuning rules, including the SVD approach, are equally difficult to apply to such a complex process.

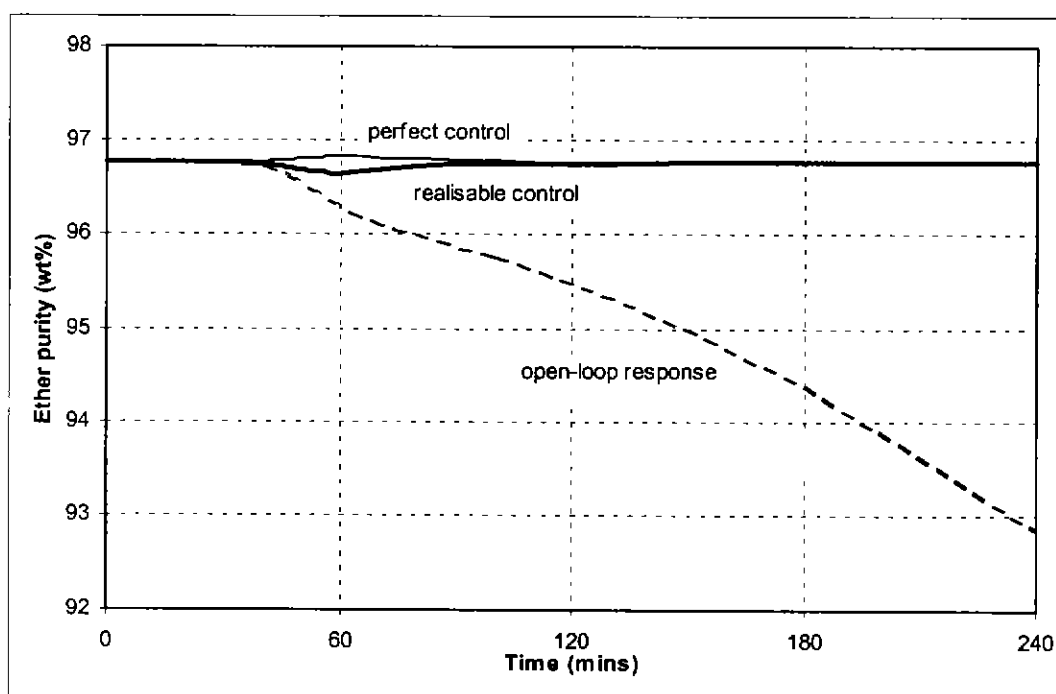
The parametric sensitivity with respect to the tuning constants was investigated by comparing the process responses to a 10% increase in feed rate under three scenarios: open-loop control (no control action so that the reboiler duty and the reflux rate remain at their initial values); combined composition and conversion control using the inferential conversion model with a set of conservative empirically defined tuning constants; and perfect control with the combination of controller and conversion model. Figures 10.3 and 10.4 show that the control performance was close to perfect with the empirically defined tuning constants. This suggests that the alternative control schemes can be effectively compared using dynamic responses that assume perfect controller performance.

The combined composition and conversion control scheme uses the stage 7 temperature to infer the ether product composition which is controlled via the reboiler duty, and an inferential model to predict the isobutene conversion which is controlled via the reflux rate. This system was benchmarked against a one-point control scheme that used the stage 7 temperature to control the product composition by manipulating the reboiler duty with a constant reflux rate. Both control schemes were assumed to operate perfectly so that the controlled variables never deviated from their set-points. Two tests were considered: a 20% increase in feed rate made over 10 minutes (Figures 10.5 and 10.6); and a 2% increase in the overall ethanol to isobutene ratio (ethanol excess) made smoothly over 60 minutes (Figures 10.7 and 10.8). In each case, composition control is achieved via the stage 7 temperature *without* cascading the set-point from a process analyser measurement. Therefore, the actual ether purity varies somewhat from the initial conditions.

The combined composition and conversion controller provides effective disturbance rejection for the increase in feed rate and significantly reduces the deviation in ether purity and isobutene conversion that would result from a one-point control scheme. Although the composition offset could have been eliminated using a cascade loop to manipulate the temperature controller set-point according to a process analyser measurement, this process

enhancement could add significant dead-time to the control loop which might worsen the overall control performance. Furthermore, the isobutene conversion would still deviate from its initial value since no adjustment would be made to the reflux rate if one-point control was used.

Two-point control was less successful in rejecting feed composition disturbances. Figure 10.7 indicates that the ether purity deviates less than with one-point control but the offset is still significant and the advantage is only incremental. Figure 10.8 shows that the inferential conversion model is unable to effectively control the isobutene conversion to a set-point. This is a result of model mismatch and an inability of the inferential model to predict the conversion for feed compositions that are significantly different to the base case. The performance of the inferential model could be enhanced in this area by collecting more data with different feed compositions but an intrinsic problem remains. This is not necessarily surprising given the difficulty of inferring composition from VLE temperature measurements in a multi-component mixture (Marlin, 1995).



**Figure 10.3 - Effect of Tuning on the Ether Purity Response to a Feed Rate Disturbance with a Combined Composition and Conversion Controller**

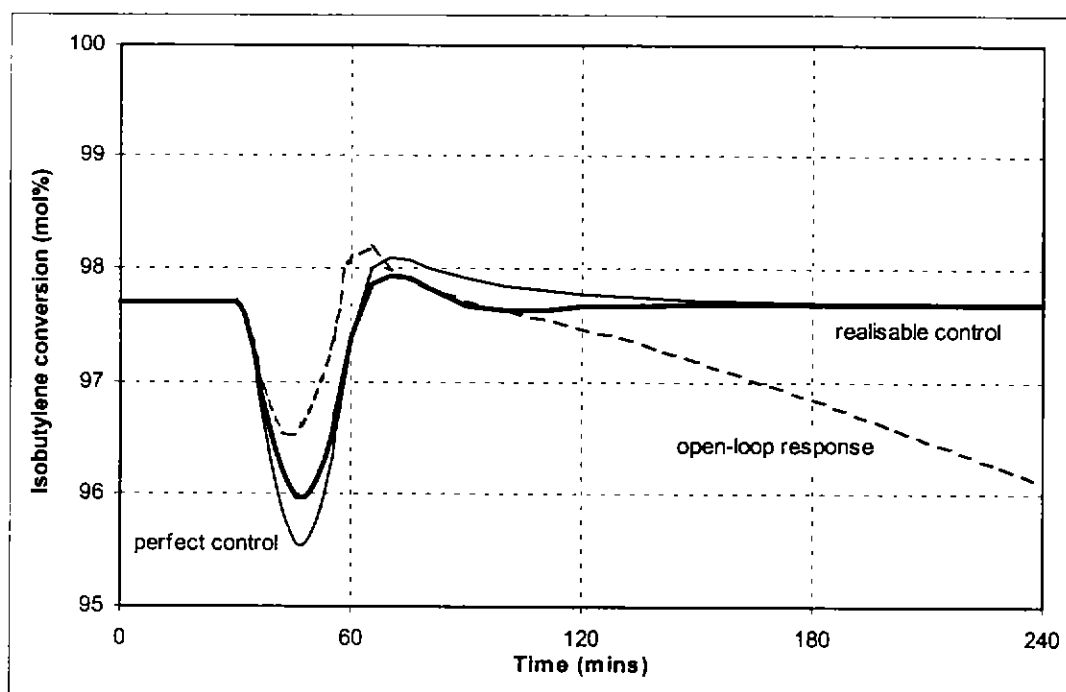


Figure 10.4 - Effect of Tuning on the Actual Conversion Response to a Feed Rate Disturbance with a Combined Composition and Conversion Controller

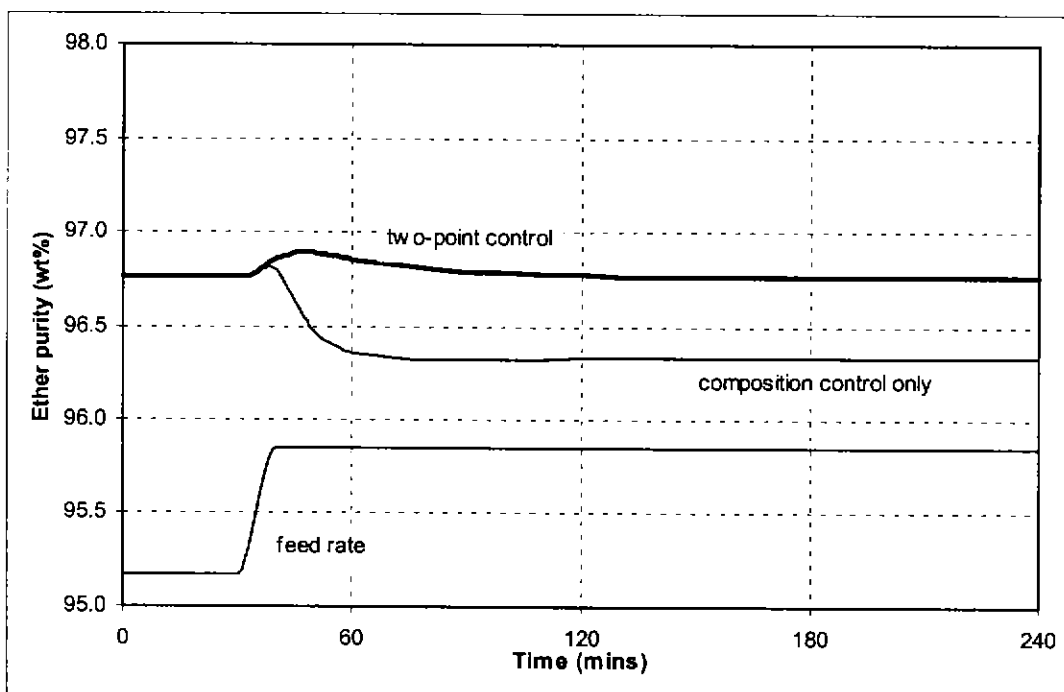


Figure 10.5 - Ether Purity Responses to a Feed Rate Disturbance with and without Combined Composition and Conversion Control



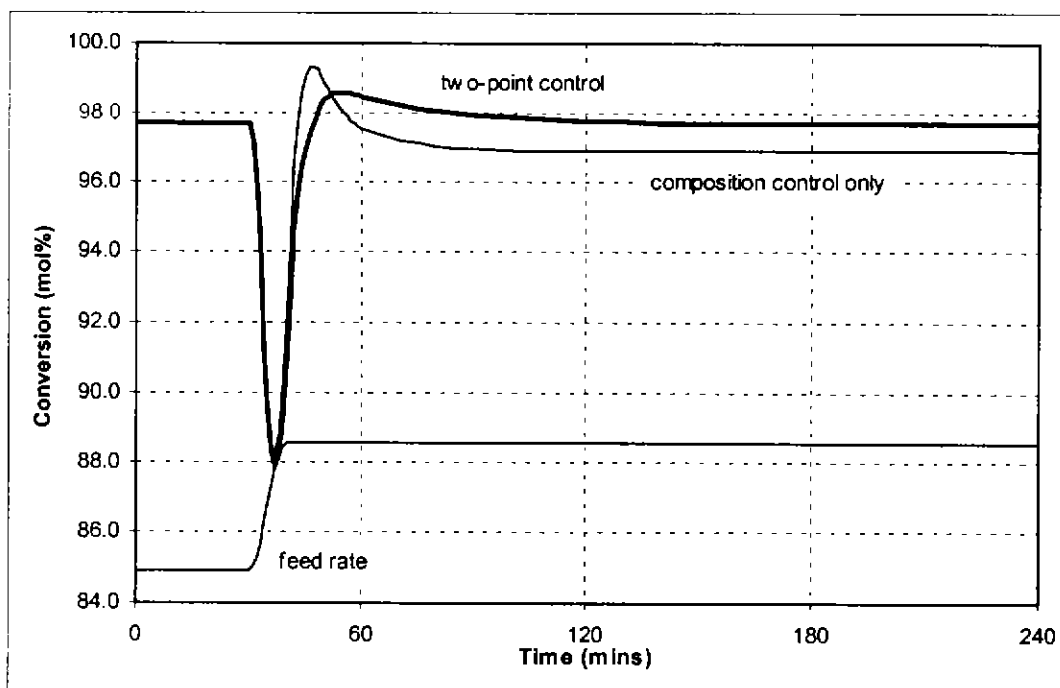


Figure 10.6 - Conversion Responses to a Feed Rate Disturbance with and without Combined Composition and Conversion Control

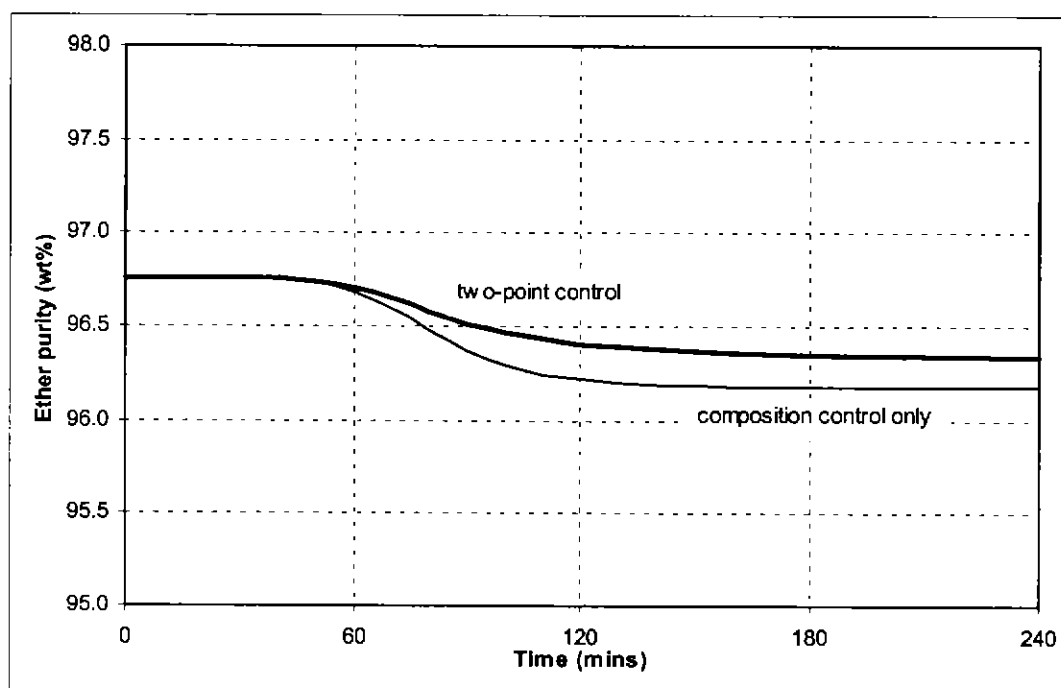


Figure 10.7 - Ether Purity Responses to a Feed Composition Disturbance with and without Combined Composition and Conversion Control

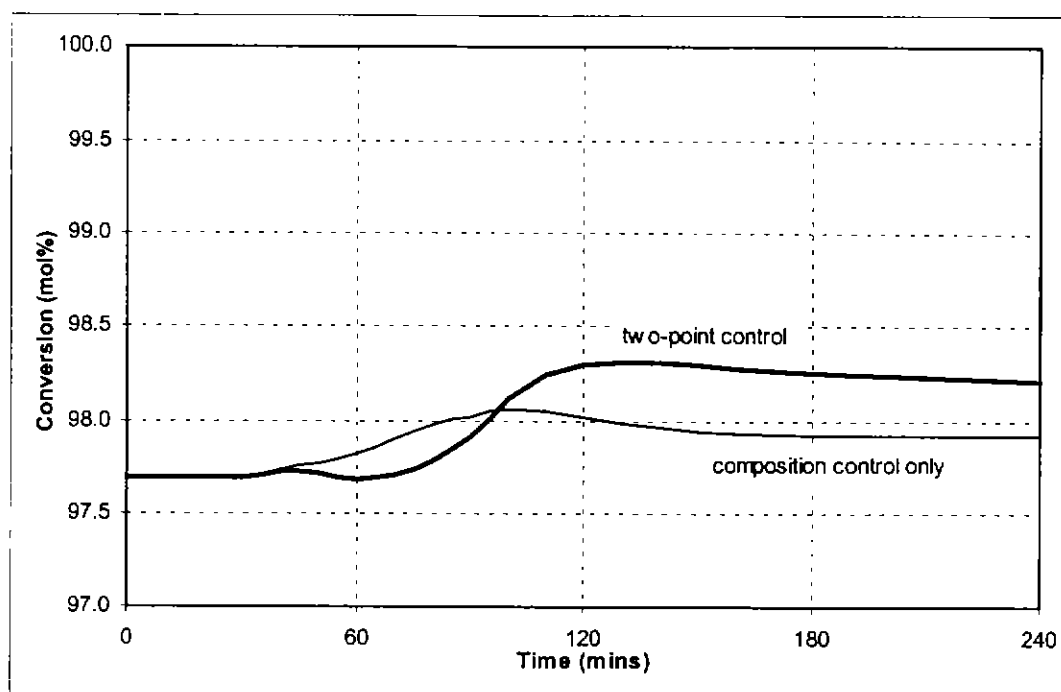
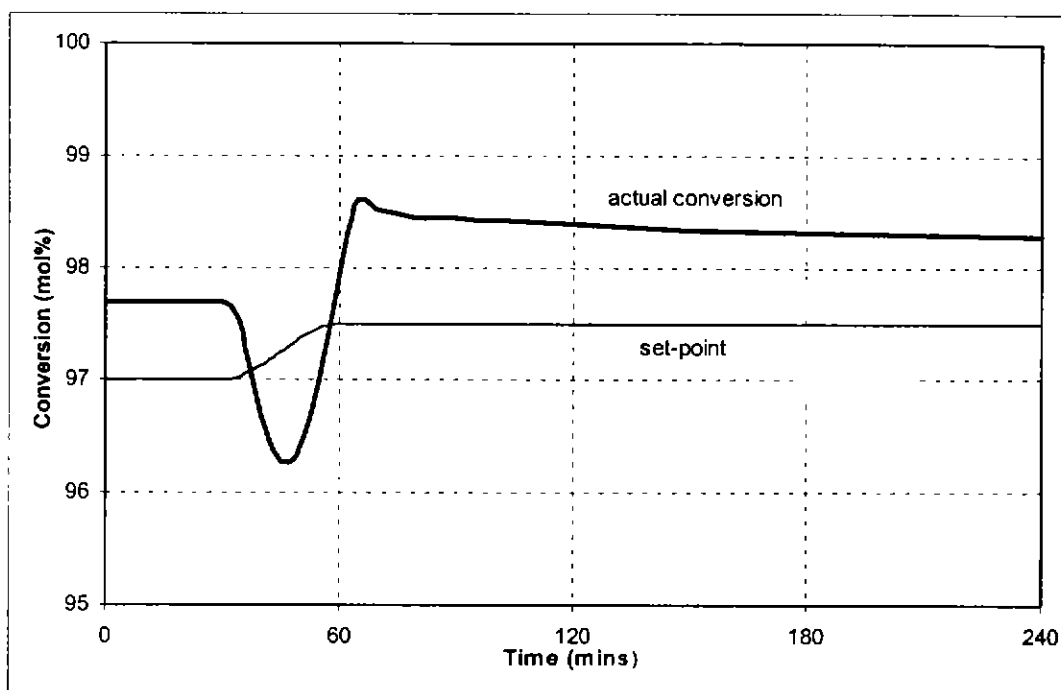


Figure 10.8 - Conversion Responses to a Feed Composition Disturbance with and without Combined Composition and Conversion Control

Although the inferential conversion model is not sufficiently accurate to allow the isobutene conversion to be controlled to a set-point, the model bias can be updated periodically (daily, if necessary) to provide adequate set-point control. The two-point control scheme can also be used to manipulate the conversion (by changing the set-point) to return the column operating conditions to the desired level. For example, if a laboratory result indicated a low isobutene conversion, the conversion set-point could be increased accordingly (by an amount equal to the difference between the measured value and the desired result) to optimise the process. Similarly, a very high conversion generally indicates that the ether purity is low or that the energy input is higher than required to meet the product quality specifications. The actual isobutene conversion could then be decreased by adjusting the controller set-point. Therefore, although set-point control is not directly realisable, techniques are available to overcome this limitation. Figure 10.9 shows that the actual conversion increases by a similar amount to the change in the set-point (0.5%). Note that the set-point is changed slowly as perfect inventory control was again assumed and a rapid change has the potential to destabilise the column operation. Note also the inverse response that potentially increases the complexity of the control problem.



**Figure 10.9 - Response to a 0.5% Increase in the Inferential Conversion Controller Set-Point**

A less obvious advantage of the two-point control scheme is implicit decoupling of the composition control loop. The one-point (composition only) control scheme suffers from the disadvantage of a low process gain between the temperature controller set-point and the ether purity so that a large change is required in the stage 7 temperature to effect a relatively small change to the ether purity. Figure 10.10 shows the effect of a 10°C increase in the temperature controller set-point with and without inferential conversion control. Reactive distillation (like conventional distillation) is an ill-conditioned process which implies that the open-loop and closed-loop gains differ significantly (often by an order of magnitude). Effectively, the process is bidirectional as there is a low-gain and a high-gain relationship for each of the manipulated variables. Inferential conversion control effectively allows the column to be operated as if the secondary manipulated variable (in this case, the reflux rate) is closed-loop. Thus, the process objective (i.e. the ether purity) is much more sensitive to changes in the primary controlled variable (i.e. the stage 7 temperature).

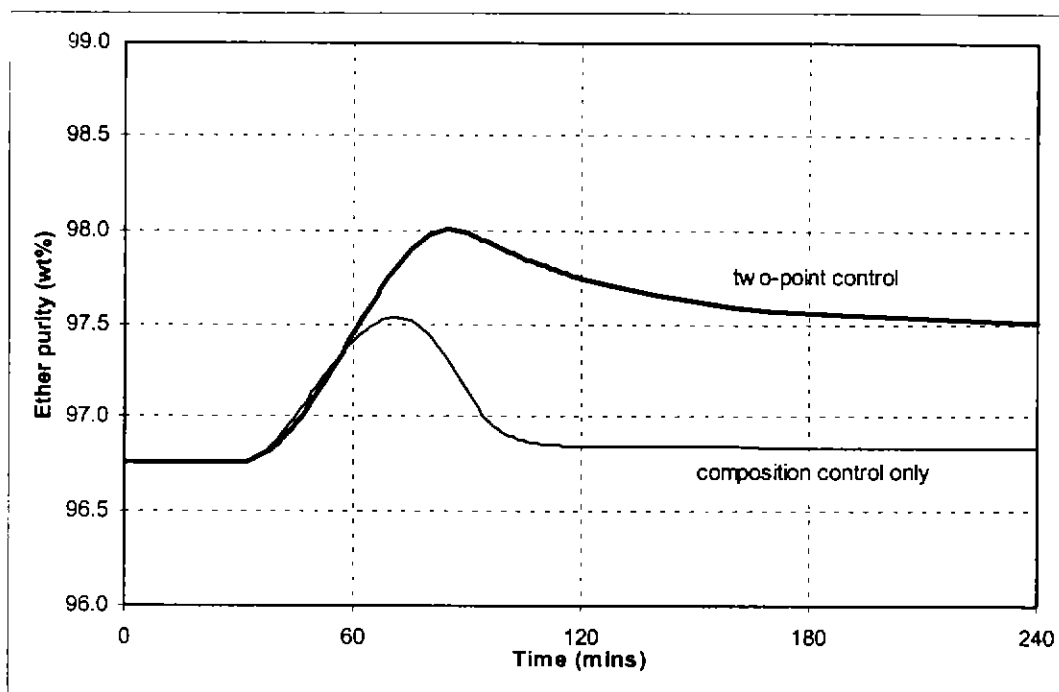


Figure 10.10 - Effect of a Composition Controller Set-Point Change on the Ether Purity with  
Combined Composition and Conversion Control

Dynamic compensation could have been added to the closed-loop inferential controller but was not essential given the effectiveness of the control system without dynamic compensation and the location of the temperature sensors relatively close to the column extremities. Furthermore, the usefulness of dynamic compensation deteriorates if the process time constants vary due to regular and/or large changes in the feed rate. Here, a packed column is advantageous as the volumetric hold-up increases to some extent with increases in the feed rate so that the changes in time constants are diminished.

#### 10.1.4 Effectiveness of Inferential Conversion Control

One-point control of the ETBE reactive distillation column using the reboiler duty (or the bottoms draw rate) to control the bottoms composition inferred via a stripping section temperature (e.g. stage 7) was found to be closed-loop stable, unlike similar control schemes that used other temperatures (e.g. the reboiler temperature) to infer the ether purity. This control scheme has good disturbance rejection properties and yields fast responses but provides only implicit control of the reactant conversion.

Isobutene conversion in this column can be predicted to within 1.0% using a statistically based inferential model and measurements of only two column temperatures (e.g. the temperature at the top of the reactive section and a temperature near the reboiler). The predicted conversion is closed-loop stable with the reflux rate, provided the bottoms

composition is also controlled in closed-loop. The combination of bottoms composition control (using a stripping section temperature, with or without set-point cascade from a process analyser) using the reboiler duty and inferential conversion control using the reflux rate produces an effective two-point control system which is appropriate for reactive distillation and, specifically, for etherification columns.

The primary advantages of combined composition and conversion control, compared with composition-only control, are:

- automated adjustment of the operating conditions to optimise isobutene conversion, and therefore to maximise profitability;
- highly effective rejection of feed rate disturbances from both the composition and inferential conversion control loops;
- tighter control of the ether composition where an inferential composition model is used (e.g. via a stripping section temperature);
- increased sensitivity in the composition control loop;
- no loss in dynamic responsiveness.

The control scheme relies on a process model to predict the conversion and the effective implementation of a composition controller. The composition controller might also rely on a secondary process measurement (e.g. a stripping section temperature) to infer the process objective (i.e. ether purity). Consequently, the control scheme has some intrinsic limitations, including a reduced effectiveness for feed composition disturbances, which is a requirement for robust and accurate temperature sensors and transmitters (especially at the top of the reactive section), and the inability to control the actual reactant conversion to a set-point without incorporating laboratory updates into the control scheme to compensate for model uncertainty. These limitations are essentially minor for most practical applications. Set-point control can be achieved using process analysers to measure various compositions directly, but the presence of measurement errors (which may be as high as the inferential model) and dead-time are detrimental, and the overall control system effectiveness is not guaranteed to be enhanced.

## 10.2 CONTROL TO COUNTERACT OUTPUT MULTIPLICITY

### 10.2.1 Open-Loop Operation

The presence of multiple steady states in reactive distillation can influence the way a reactive distillation column should be operated and controlled. Transitions between parallel steady states were discussed in Chapter 8 (Section 8.4) and it was shown that the column conditions and product compositions can change without any change in the manipulated variables used for composition control. For example, some perturbations in either the feed rate or the feed composition can initiate subtle changes in the composition profile, which results in the column stabilising to a new steady state. While the feed rate is unlikely to change without warning, the feed composition might be reasonably expected to vary due to the effects of upstream processes and raw materials (e.g. crude oil) compositions. This immediately creates an incentive to avoid open-loop operation if multiple steady states are possible.

A steady state transition is also possible if both the feed rate and feed composition are constant. In this case, a perturbation in an external stream can initiate the sudden change. For example, the reboiler duty is often manipulated (indirectly) by regulating the steam flow to the reboiler. Since the duty that is obtained from this arrangement depends on both the steam flow and the steam pressure, a slight decrease in the supply pressure will result in a decrease in the reboiler duty even if the flow rate is not changed. Thus, an unobserved perturbation in the steam pressure could result in a transition from a desirable to an undesirable steady state even if the feed rate, feed composition, reflux rate and steam rate to the reboiler are constant. This possibility provides a further motivation for implementing closed-loop composition control of at least one product.

### 10.2.2 Inventory Control

A fundamental assumption that is often made in the analysis of distillation control structures is perfect (or nearly perfect) inventory control. This reduces the full 5 x 5 control system to a 2 x 2 system and, thereby, substantially simplifies the controller design. This assumption is usually valid as the pressure and level control loops are normally fast acting and globally stable. Indeed, this assumption is always acceptable if a product stream is used to control the levels in the reflux accumulator and the reboiler sump.

However, if the level controller is paired with an internal flow (e.g. the reflux or boilup rate), the stability is only ensured if the following conditions are satisfied for the reflux accumulator (inequality 10.4) and reboiler sump (inequality 10.5):

$$\frac{\partial h}{\partial L} < 0 \quad \forall L \quad (10.4)$$

$$\frac{\partial h}{\partial Q_R} < 0 \quad \forall Q_R \quad (10.5)$$

Considering the reflux accumulator only, inequality (10.6) holds for all values of the reflux rate so that inequality (10.4) can be extended to produce inequality (10.7) which is a necessary condition for the global stability of a linear (e.g. PI) level controller.

$$\frac{\partial h}{\partial D} < 0 \quad (10.6)$$

$$\frac{\partial D}{\partial L} > 0 \quad \forall L \quad (10.7)$$

Similarly, inequality (10.8) can be derived as a linear stability condition for the reboiler sump level controller.

$$\frac{\partial B}{\partial Q_R} > 0 \quad \forall Q_R \quad (10.8)$$

The converses of inequalities (10.7) and (10.8) (i.e. positive values of the derivatives for any value of the reflux rate or reboiler duty) describe necessary geometric conditions for output multiplicity. Therefore, wherever output multiplicity exists, at least one of the level control loops will not be globally stable if a linear level controller is used with an internal flow. This creates a strong incentive to use an energy balance control configuration (e.g. the LV scheme) for reactive distillation.

Interestingly, there is no evidence of output multiplicity in non-reactive distillation where a material balance control structure (e.g. DV, LB, etc.) is used unless the associated level control is very poor (Jacobsen and Skogestad, 1994). This result appears to extend to reactive distillation although pseudo-multiplicity has been detected with a material balance control configuration. This suggests that a material balance control configuration could be useful to avoid possible transitions between parallel steady states where they exist but such a scheme can not be implemented with linear level controllers. It is also doubtful whether a complex non-linear controller could adequately account for the observed behaviour in order to satisfactorily control the column inventory near unstable operating points (i.e. where unplanned steady state transitions are possible).

This apparent paradoxical situation creates a dilemma for control system design. If an energy balance control structure is used, multiple steady states can occur and there is the possibility of unwanted transitions from desirable to undesirable steady states. However, if a material balance structure is used, only one steady state is possible but satisfactory control of the column inventory is unlikely and this could ultimately lead to equipment failures or the complete shut down of the column. The events that trigger a transition in the first case and destabilisation in the second case are likely to be similar (e.g. feed rate or composition perturbations, or disturbances to external variables such as the steam pressure or cooling water temperature). The lesser disaster is probably an unwanted transition as it should be possible to recover the original operating state with an appropriate response from the process operator. Techniques for achieving the return to the desirable steady state are discussed in the next section.

### **10.2.3 Programmed Transitions**

#### *10.2.3.1 Motivation*

A column that exhibits multiple steady states could reach an undesirable steady state during a period of open-loop operation or as a result of an inappropriate start-up procedure. Open-loop operation is necessary to tune controllers, calibrate transmitters, etc. and makes the column vulnerable to an unwanted transition that might result from a transient disturbance (perturbation). A poorly managed start-up could also allow a column to stabilise at an undesirable steady state. Although the implementation of a device (e.g. a monitoring system for the product yield or temperature which is connected to an alarm or warning) to detect an unwanted steady state should be straight forward, a method for returning the column to the coveted conditions must be established.

The mechanism for completing the return transition should use only the available manipulated variables and avoid any risk of destabilising the column, for example, rapid changes in the internal flow rates or detrimental interactions with the inventory controllers. Ideally, the transition would also be achieved quickly and smoothly with minimal operator intervention. Possible means of achieving this objective include:

- a) perturbing the column in a controlled manner in order to promote a transition to the desirable steady state;
- b) confining the column operation to a single steady state by initiating closed-loop control of a suitable temperature;
- c) forcing a change in the column material balance by manipulating a product draw rate;



- d) adjusting the primary manipulated variable until a catastrophic shift occurs.

These alternatives are evaluated below for implementation on the MTBE column described in Chapter 8. This column was selected because it has already been shown to exhibit multiple steady states in the significant operating range.

### 10.2.3.2 Controlled Perturbation

A suitable perturbation in the feed rate, feed composition or either of the manipulated variables being used for composition control (the other manipulated variables should be retained in closed-loop control of the column inventory) might be effective in producing the desired steady state transition. However, the feed rate and composition are normally determined by external factors (e.g. product demand and upstream processes) so that it would be preferable to use one of the manipulated variables to force the transition.

The simulation results included in Chapter 8 did not include a case where a reboiler duty perturbation produced a steady state transition from the low conversion steady state so that a solution is not immediately evident. However, the simulation results can be used to calculate the net amount of heat contained within the column to determine whether differences between the steady states might be offset by an energy impulse (i.e. reboiler duty perturbation). The required relationship is shown in equation (10.9), where  $\tilde{H}$  is the total energy contained within the column,  $M$  is the hold-up on each stage,  $H$  is the specific enthalpy on each stage and  $n$  is the number of stages (including the condenser and reflux accumulator, and the reboiler sump).

$$\tilde{H} = \sum_{i=1}^n M_i H_i \quad (10.9)$$

Evaluation of equation (10.9) for parallel steady states of this MTBE column indicates that the low conversion solution contains the most energy while the high conversion solution contains the least energy. This suggests that a temporary decrease in the energy input to the column might initiate a transition to the high conversion steady state. The difference in heat content is approximately 110 MJ, which is equivalent to a perturbation of 5 kW (approximately 10%) for 360 minutes at the base case feed rate of 2.75 kmol/hr. Unfortunately, such a large perturbation produced very rapid changes in column properties and prevented a complete solution during simulation. This perturbation might also result in process instability in practice. Even comparatively small perturbations (e.g. 2.8 kW over 60

minutes, equivalent to an energy impulse of -10 MJ) prevented the simulation from converging. This testifies to the sensitivity of the column operation and suggests that manual control of this column would be difficult.

The observed sensitivity is a result of a domino effect that is initiated by an energy impulse. The reactive section is affected most significantly: the initial change in the heat input produces a change in the composition profile which then affects the reaction and changes the heat balance (via a change in the net heat of reaction) which has a further effect on the composition profile. Simulations indicated that, generally, imparting a small perturbation allows the column to return to the original operating conditions while a larger perturbation produced instability caused by the formation of a dry stage(s) within the column. Although a suitable perturbation might exist, this method of forcing a transition was considered impractical due to the degree of precision required and the risk of destabilising the column operation.

Reflux rate perturbations were also found to be ineffective in forcing a steady state transition. As with the reboiler duty, small perturbations resulted in the column returning to the original steady state after the transient response or produced sufficiently rapid changes in the column properties to prevent a complete dynamic solution. The simulation results suggest that a controlled perturbation in a manipulated variable is not a practical method of forcing a steady state transition.

#### *10.2.3.3 Closed-Loop Control*

The possibility of using closed-loop operation to manage a transition between parallel steady states appears to have some potential. Theoretically, the column inputs could be manipulated in order to achieve a specified output condition that was only found in the desirable steady state. For example, a high reboiler temperature and moderate stripping section temperature are characteristics of the high conversion solution so that either of these variables could potentially be controlled to force a transition.

However, as described above, the relationships between potential manipulated and controlled variables place restrictions on the performance of linear controllers. Robust control of the reboiler temperature is not possible as the process gain changes sign in the interval around the normal operating point. Although an effective controller for  $T_{12}$  is easier to develop, global stability is not possible for the medium conversion solution unless the controller gain changes sign at the singular points. Thus, a finely tuned adaptive controller is required. Finally, the controller must be capable of both increasing and decreasing the

manipulated variable in the course of a single set-point update in order to return the column inputs to the original values after the steady state transition has been completed. An adaptive controller is a technically feasible method of programming a steady state transition but is unlikely to be a practical solution due to the required accuracy of the model and the complexity of the continuation path (via an unstable, medium conversion steady state) which must be followed.

#### *10.2.3.4 Material Balance Manipulation*

The manipulation of the column material balance via a product draw rate was also considered as a method of programming a transition. A temporary reassignment of manipulated variables is required if the LV configuration (the preferred control structure) is in use as neither the reflux rate nor the reboiler duty can affect the material balance directly. If the material balance change is to be affected using the bottoms draw rate, the reboiler sump level must be temporarily controlled via the reboiler duty. Tight level control is also required to ensure that the changes in the bottoms rate are transmitted directly to the column and are not absorbed by inventory changes.

Whereas previously a perturbation in a manipulated variable was required, here the shift must be permanent as the bottoms rate is different for each steady state. This was tested using dynamic simulations of the MTBE column. The bottoms rate was ramped over a period of 60 minutes from the low conversion steady state value ( $0.0935 \text{ m}^3/\text{hr}$ ) to the high conversion steady state value ( $0.1181 \text{ m}^3/\text{hr}$ ). The column responded in the desired manner and a transition to the high conversion steady state was completed after about eight hours, as shown in Figure 10.10. The reboiler duty (for perfect level control of the reboiler sump) varied both above and below the steady state value during the transition, as shown in Figure 10.12.

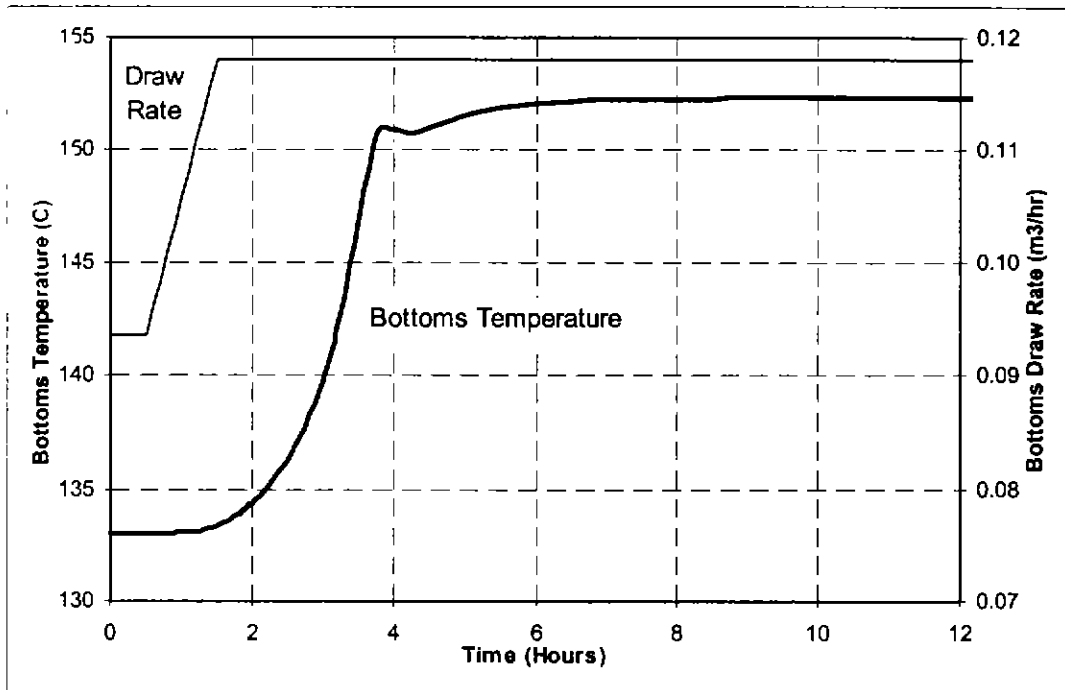


Figure 10.11 - Steady State Transition by Material Balance Manipulation

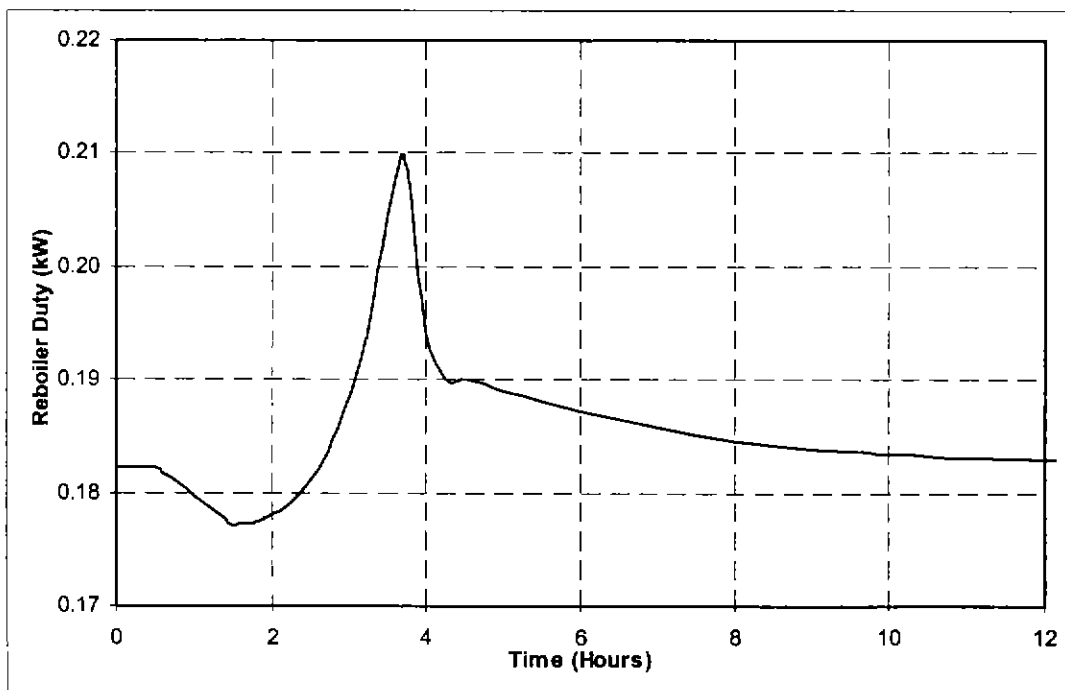


Figure 10.12 - Reboiler Duty Response During a Programmed Transition

Perfect level control is not always practically possible. Does the steady state transition still occur if the level control is imperfect? Steady state simulations can be used to generate the continuation curve for the reboiler duty as the bottoms rate is varied from 0.0935 to 0.1181 m<sup>3</sup>/hr. This was done and is shown in Figure 10.13. The continuation path moving from the low conversion steady state (point A) through the medium conversion steady state (point B)

to the high conversion steady state (point C). The shape of the path resembles the reboiler duty responses shown in Figure 10.12.

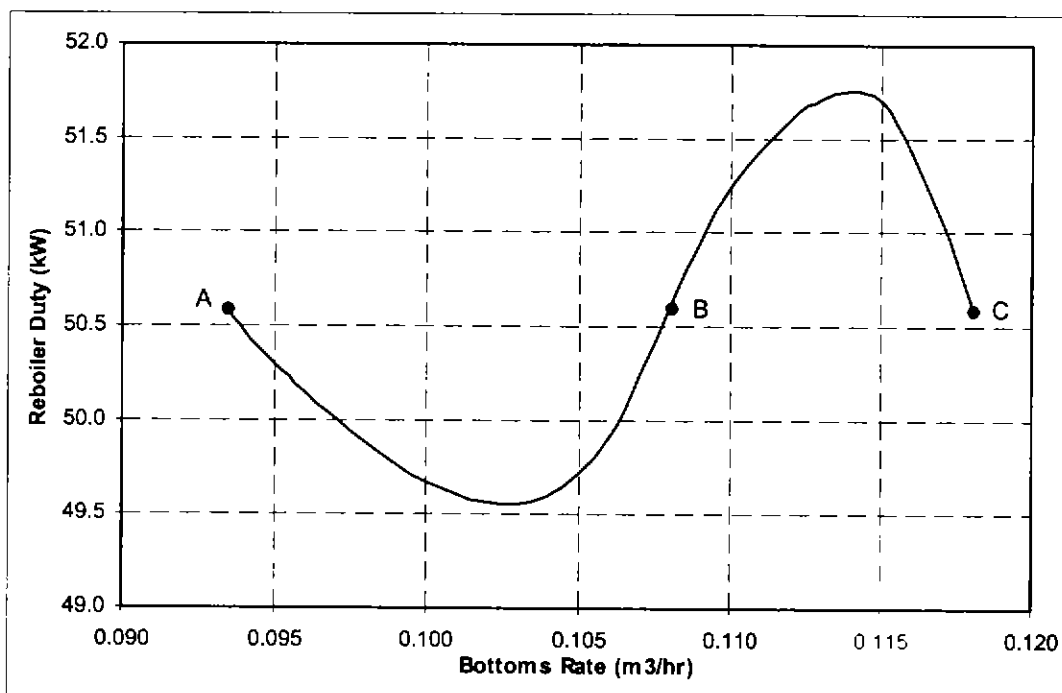


Figure 10.13 - Reboiler Duty Continuation Path

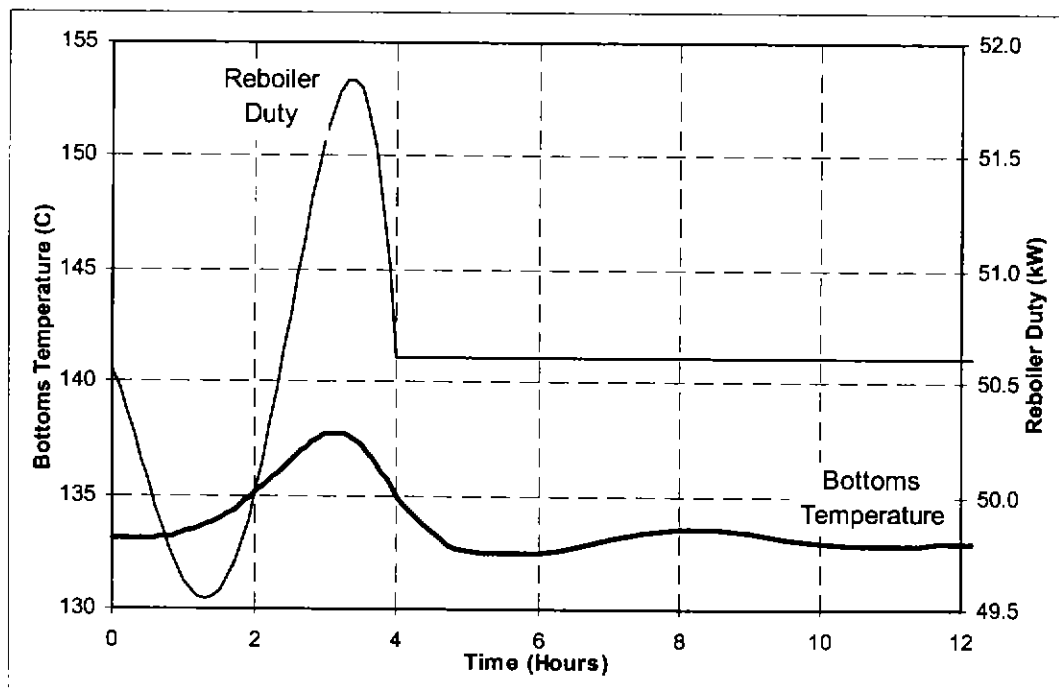


Figure 10.14 - Programmed Transition Using Reboiler Duty

A fourth order polynomial regression was found to produce a good fit for the continuation path ( $R^2 > 0.99$ ). If the reboiler duty is programmed to respond according to the regression

function over a period of 240 minutes, the bottoms temperature ( $T_b$ ) responds as shown in Figure 10.14. The column restabilises to the low conversion steady state. Therefore, while a planned manipulation of the column material balance can be used to transfer the operating point between parallel steady states, perfect level control is a prerequisite for a successful transition. Thus, manipulation of the bottoms rate is also not a practical method of promoting a steady state transition.

Material balance manipulation via the distillate product draw is also unviable due to the difficulties in maintaining perfect level control of the reflux accumulator. Once again, a linear controller is incapable of providing perfect level control as the manipulated variable (the reflux rate) must be both increased and decreased during the steady state transition.

#### *10.2.3.5 Catastrophic Shift*

Multiple steady states only exist for this column for finite ranges of the column inputs: there are three steady states for reboiler duties between 49.6 kW and 51.8 kW but only one steady state for reboiler duties outside this interval. Therefore, if the column is operating at the low conversion steady state with a reboiler duty of, say, 50.6 kW, decreasing the duty to a value below 49.6 kW without changing any other input will force a catastrophic shift in the column operating point. Increasing the reboiler duty again should move the operating point along the continuation path to the high conversion steady state, regardless of the starting point. Note that the reboiler temperature will only change slightly during the catastrophic shift but that other temperatures, the internal flow rates and the stage-to-stage compositions will all change dramatically.

Other column inputs can also be manipulated in this manner to affect catastrophic shifts. For example, from the low conversion initial state described above, increasing the reflux rate to 1.25 m<sup>3</sup>/hr would have a similar affect to decreasing the reboiler duty. Reversing this change should complete a steady state transition to the high conversion steady state. Similarly, a transition in the opposite direction could be enforced by increasing the reboiler duty to affect a catastrophic shift and then reversing the change to allow the column to move along the continuation path and restabilise at the low conversion steady state.

Unfortunately, as the name suggests, the catastrophic shift might temporarily destabilise the column due to the rapid changes in the internal flow rates. However, this appears to be the only effective method of guaranteeing a transition between parallel steady states.

## 10.3 INTEGRATED CONTROL SCHEMES

### 10.3.1 Changing Process Objectives

It has already been suggested that a vital first stage of control system design is to accurately and appropriately determine the control objectives so that the process performance is optimised for some given economic constraints. In many cases, this step is neglected to the detriment of the controller's effectiveness. An important consideration in this regard is that it is normal for the economic constraints to shift periodically and that this can affect the control objectives both quantitatively and qualitatively. Indeed, a single set of control objectives may not be satisfactory.

The management of the control objectives in response to changing economic conditions is illustrated here for the 10 stage ETBE column described previously. The two most important process parameters for this column were considered to be the ETBE purity in the bottoms product and the isobutene conversion. In other columns, the ethanol concentration in the distillate (or another process parameter) could be highly important, and a different control system would be required. However, the current assumption of purity and conversion targets provides adequate scope for the exploration of an integrated control scheme designed to reflect the variation in economic values. Three different operating modes were considered in order to allow the process profitability to be maximised under a wide range of conditions.

The first mode of operation controls both the bottoms purity and isobutene conversion to pre-determined targets that correspond to downstream processing requirements or the results of a plant-wide optimisation. In the second mode, the bottoms purity is still controlled to a pre-determined target but the second control parameter is used to maximise the reactant conversion. In the third mode, both the purity and conversion are maximised using the two available degrees of freedom.

### 10.3.2 Control Structure

Although the control objectives have been established, the actual controlled variables and manipulated variables are still to be decided. Many choices are available but the most likely candidates for the controlled variables are the various flows, temperatures, pressures and compositions in the system. However, the final choice is not restricted to these parameters and the use of composite variables such as the column flooding factor or the energy consumption could be advantageous for some economic scenarios. The manipulated variables are effectively selected in choosing the control structure that will be used.

A control structure which adequately supports all three control modes is required. Although the specific controlled variables have not yet been selected for each mode, some general properties of the various control configurations allow a satisfactory selection to be made forthwith.

The energy-balance control configurations (e.g. LV) manipulate the internal liquid and vapour flows, which affect the feed-split and fractionation immediately and directly, while the material-balance configurations (e.g. DV, LB, etc.) manipulate external variables (i.e. the product flow rates) and rely on these changes being transmitted to the column via the level control loops. These level control loops should be stable and in near-perfect control in order to maintain good dynamic responsiveness with a material-balance control structure. Conditions for the stability of the inventory controllers (with linear control algorithms) were derived in Section 10.2.2 and it was concluded that these conditions do not hold for the material-balance control configurations where output multiplicity exists. Although output multiplicity was not detected in this particular column, the presence of multiple steady states in other similar columns (both MTBE and ETBE) suggests that the selection of an energy-balance structure would be prudent.

This configuration is very widely used in industrial practice for non-reactive distillation. The considerations described above suggest that it is likely to be widely used for reactive distillation too and this was confirmed for open-loop, one-point and two-point control of the 10 stage ETBE column in Chapter 9 and Section 10.1.

### **10.3.3 Operating Modes of the Integrated Controller**

#### *10.3.3.1 Control Mode 1*

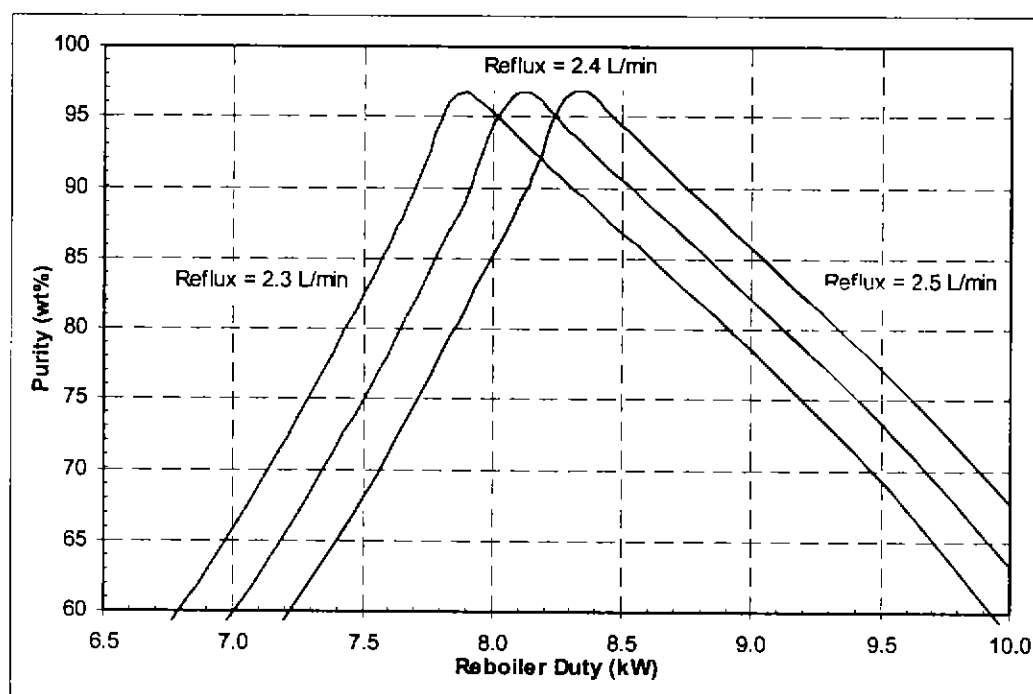
The ETBE purity and the isobutene conversion must both be controlled to specified targets in this mode. Ideally, this would be best achieved using direct measurements of the two control objectives in order to avoid the uncertainty that is associated with an inferential indication. However, this approach is impractical with linear controllers.

The limitations of using a direct measurement of the ETBE purity (or the conversion) have been discussed previously for both one-point and two-point controllers and mostly derive from the input multiplicity which is present between the controlled and manipulated variables. This is clearly shown in Figure 10.15 where the process gain between the bottoms composition and the reboiler duty can be both positive and negative at a constant reflux rate. This property is also observed if the reflux rate is used as the manipulated variable. The pairing with reflux rate also suffers from the increased physical distance

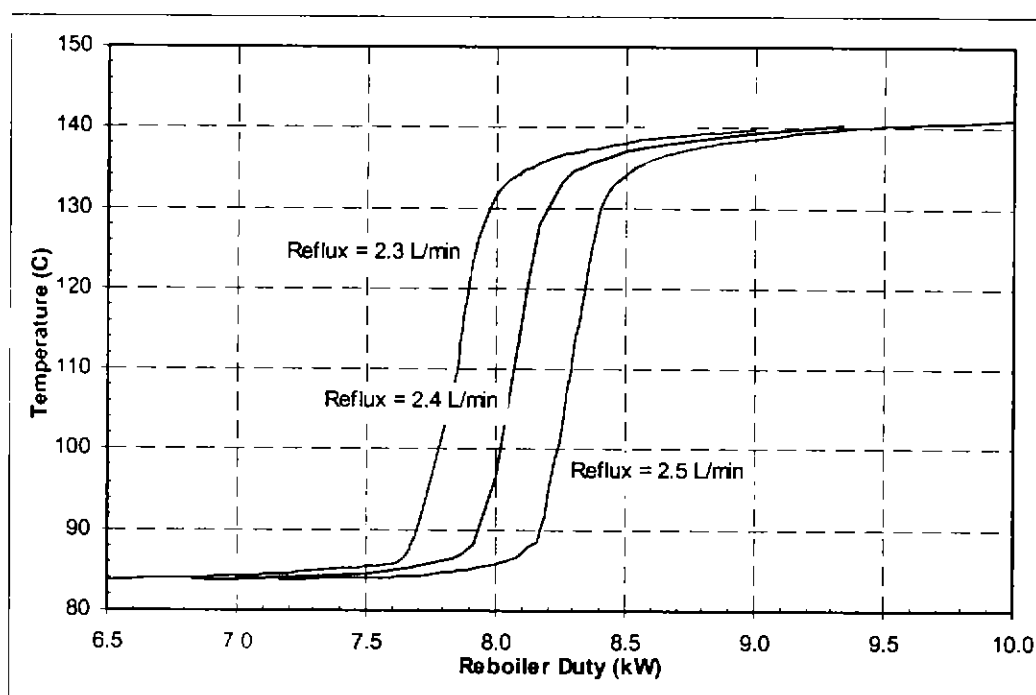


between the point at which the purity is measured and the location of the final control element that leads to a less dynamically responsive system.

A technique for avoiding the input multiplicity was proposed in Chapter 9. Essentially, a temperature from near the middle of the stripping section (e.g. stage 7) is controlled instead of the reboiler temperature or composition. This results in the one-to-one relationship shown in Figure 10.16, which has much better characteristics for controllability. The selected temperature could either be used directly or within a cascade loop where the master controller measured the ETBE purity and updated the set-point of the temperature controller. This arrangement is more effective than using the analyser output directly but could still not be globally stable due to the input multiplicity that persists.



**Figure 10.15 - Effect of Reboiler Duty on the ETBE Purity**



**Figure 10.16 - Effect of Reboiler Duty on Mid-Stripping Section Temperature**

The control of the isobutene conversion presents a more difficult measurement problem. Direct measurements would require a substantial amount of data and equipment. The use of several easily measured temperatures to predict the conversion was demonstrated in Section 10.1. This is valid and could be used to produce good control. However, a simpler model that uses only the maximum and minimum reactive section temperatures was used here. Figure 10.17 shows the pattern of the relationship between the reaction zone  $\Delta T$  and the isobutene conversion for various operating conditions, with the ETBE purity control loop opened (i.e. fixed reboiler duty) and closed (i.e. fixed stripping section temperature).

The open-loop relationship includes a peak at around  $4.0^{\circ}\text{C}$  and is, therefore, bidirectional. However, temperature differentials below this value correspond to low values of the ETBE purity in the bottoms product and, therefore, are not likely operating points. Above the critical temperature differential, the relationship is smooth and monotonic. The closed-loop relationship is smooth and monotonic (and nearly linear) for all operating points of practical interest. Thus, the inferential indication of the reactant conversion provided by the reaction zone temperature differential is suitable for closed-loop control. The reaction zone  $\Delta T$  varies nearly linearly with the reflux rate for a constant reboiler duty so that stable and robust control of the conversion should be possible with this pairing.

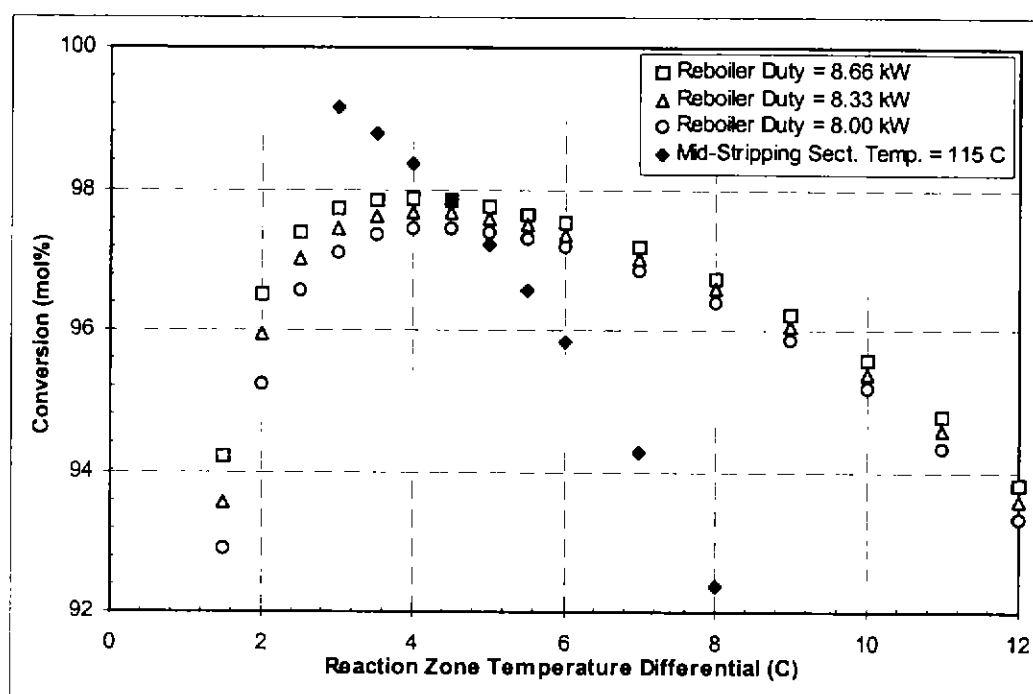


Figure 10.17 - Link Between the Reaction Zone  $\Delta T$  and Conversion

The two control loops (TC: reboiler duty-stripping section temperature; and,  $\Delta TC$  reflux rate-reaction  $\Delta T$ ) interact strongly as indicated by the relative gain which has a value of 20-60 in around the desired operating point. This is high, but comparable to a high-purity, non-reactive distillation process. Although this interaction reduces the process controllability, satisfactory closed-loop performance was achieved (see Section 10.3.4).

This control mode should be used when: (1) there are specific limits on the allowable concentration of  $C_4$  and/or ethanol in the bottoms product; (2) there is a significant cost penalty associated with giveaway (i.e. there is an economic incentive to incorporate as much  $C_4$  or ethanol in the bottoms product without violating the specification limit); and (3) the benefit of producing additional ETBE from isobutene must be optimised with the cost of the additional energy consumption (via both the heating and cooling utilities).

### 10.3.3.2 Control Mode 2

In this mode, the ETBE purity in the bottoms product is controlled but the isobutene conversion is maximised to equipment constraints. The first control loop, TC, is unchanged from the first control mode. The reflux rate is the manipulated variable for the second loop but a new controlled variable must be found. Many different equipment constraints could be active but two common constraints (in a well designed column) are flooding and the reboiler duty. Composite variables could be built to approximate both of these values (neither is easy to measure directly) in order to control the column operation close to the

appropriate limit. However, the reflux rate is nearly proportional to both these limits, regardless of the feed rate, and effective constraint management is possible by simply controlling the reflux rate directly.

This control mode is appropriate when: (1) there are limits on the bottoms product composition; (2) giveaway must be minimised concentration; and (3) the cost of additional energy consumption is always less than the value of producing additional ETBE.

#### *10.3.3.3 Control Mode 3*

The third control mode manipulates the reboiler duty and reflux rate in order to maximise the ETBE purity and to maximise the isobutene conversion. As demonstrated above, (manually) adjusting the reflux rate to close to the equipment constraints effectively maximises conversion. There is no comparable method of maximising ETBE purity because the process gain (between purity and reboiler duty) changes sign (see Figure 10.15). An optimum reboiler duty must be found.

A steady-state process model was used to find the optimal value of the mid-stripping section temperature for various feed rates and feed compositions. Surprisingly, the feed composition has a negligible effect on the optimisation results. This is fortunate since the composition is difficult to measure and less suitable for closed-loop control than flows and temperatures, etc. The simple model given by equation (10.10) was found to describe the relationship between the optimum temperature and the feed and reflux rates. This model was incorporated into a feed-forward controller (SPC) to update the temperature set-point on-line.

$$\text{Optimum TC set-point} = 121.2 + 9.2 (\text{Reflux/Feed} - 0.329) \quad (10.10)$$

Although the performance of this control loop could be enhanced by dynamic compensation so that the set-point was updated at an appropriate time after a change in the feed or reflux rates, the optimal characteristics of a lead-lag unit vary strongly with the operating conditions. Therefore, only the steady-state model was implemented on the simulations.

This control mode is recommended when: (1) there is a cost penalty associated with any reduction in the purity of the ETBE product; and (2) the value of additional conversion is always higher than the required increase in energy consumption. Intuitively, this control mode would appear attractive but is probably less likely to be used in practice as specific

targets which correspond to a global, plant-wide optimisation should yield a higher overall profitability.

The three different control modes can be implemented using only three control loops, as described above. The column operation can be changed from one mode to another by simply opening or closing particular loops, according to Table 10.5. A tick mark indicates that the control loop should be operated in *automatic* while a cross mark indicates that the loop should be operated in *manual* in order to realise the correct process objectives.

**Table 10.5 - Operation of the Individual Control Loops for Each Control Mode**

	Control Mode 1	Control Mode 2	Control Mode 3
ETBE purity is...	<i>controlled</i>	<i>controlled</i>	<i>maximised</i>
Isobutene conversion is...	<i>controlled</i>	<i>maximised</i>	<i>maximised</i>
<b>Control Loop</b>			
TC - temperature control of the mid-stripping section	✓	✓	✓
ΔTC - control of the reaction section temperature difference	✓	✗	✗
SPC - Set-point optimiser for TC	✗	✗	✓

#### 10.3.4 Controller Performance Tests

The integrated controller was implemented on the ETBE column within the SpeedUp™ dynamic simulation environment. The control loops were all tuned using recommended settings for approximate first-order-plus-dead-time (FOPDT) models which were fitted to step responses (Ogunnaike and Ray, 1994). Although these models were a poor fit in some cases and there was a high degree of non-linearity in most cases (as judged by the differences in the responses to positive and negative perturbations), the resulting values of gain and integral time (no derivative component was included in any of the controllers) were adequate to achieve satisfactory tuning. For example, some increase in the control action was tolerable before the controller became unstable. Aggressive tuning is not appropriate for this system because of its inherent non-linearity and bidirectionality.

The disturbances that are most likely to affect the process are feed rate changes and feed composition changes. The impact of other disturbances (e.g. the temperature of the heating medium to the reboiler) can be attenuated using appropriate cascade controllers and other

standard control techniques. On this basis, three performance tests were characterised for this system:

- (1) 10% feed rate increase at time = 0 minutes, followed by a 20% feed rate decrease at time = 120 minutes;
- (2) 5% increase in the stoichiometric ratio at time = 0 minutes, followed by a 10% increase in non-reactive components at time = 120 minutes;
- (3) 5°C increase in the set-point of the mid-stripping section temperature controller at time = 0 minutes, followed by a 1°C decrease in the set-point of the reaction zone temperature controller (where applicable) at time = 120 minutes.

In each case, the changes were scheduled over 5 minutes (rather than using pure step changes) to preserve continuity and to more closely simulate a real process disturbance.

The open-loop effects of the feed rate and feed composition disturbances are shown in Figures 10.18 and 10.19. Significant deviations from the initial operating conditions are seen in both cases. The processes are open-loop stable but steady state was not reattained before the second feed rate disturbance even though an additional hour was allowed. The response shown in Figure 10.18 emphasises the non-linearity and bidirectionality of the process. An increase *and* a decrease in the feed rate reduce both the ETBE purity and the isobutylene conversion. Thus, an optimum feed rate exists for the base case combination of reflux rate and reboiler duty and the process gain changes sign (i.e. the process is bidirectional). The shapes of the responses are also different, indicating strong non-linearity.

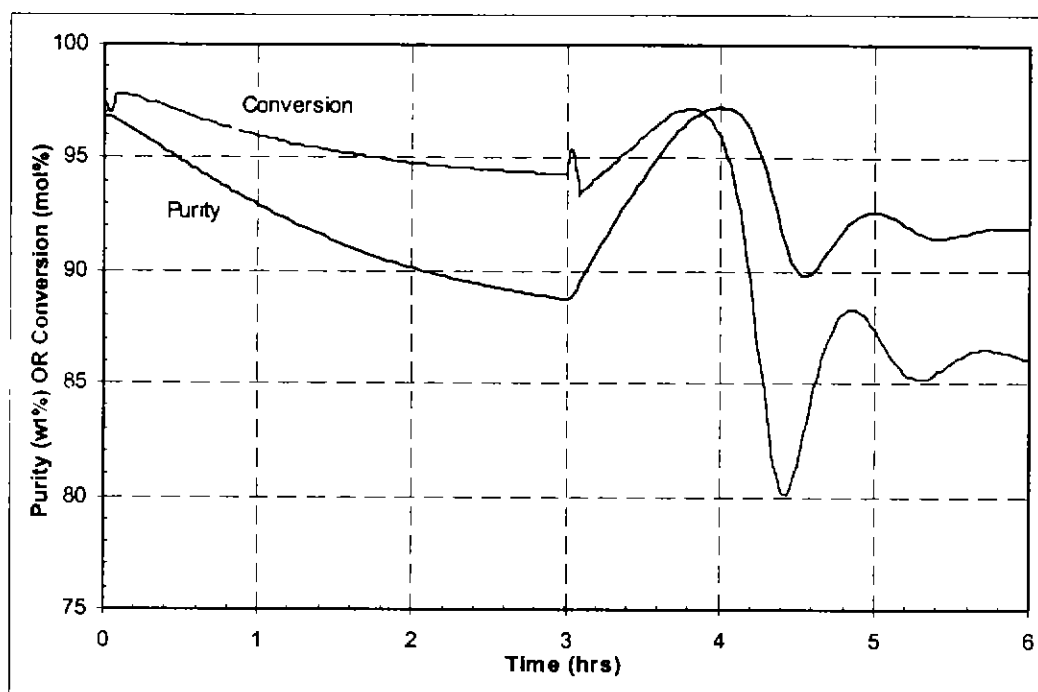


Figure 10.18 - Open-Loop Response to Feed Rate Disturbances (Performance Test 1)

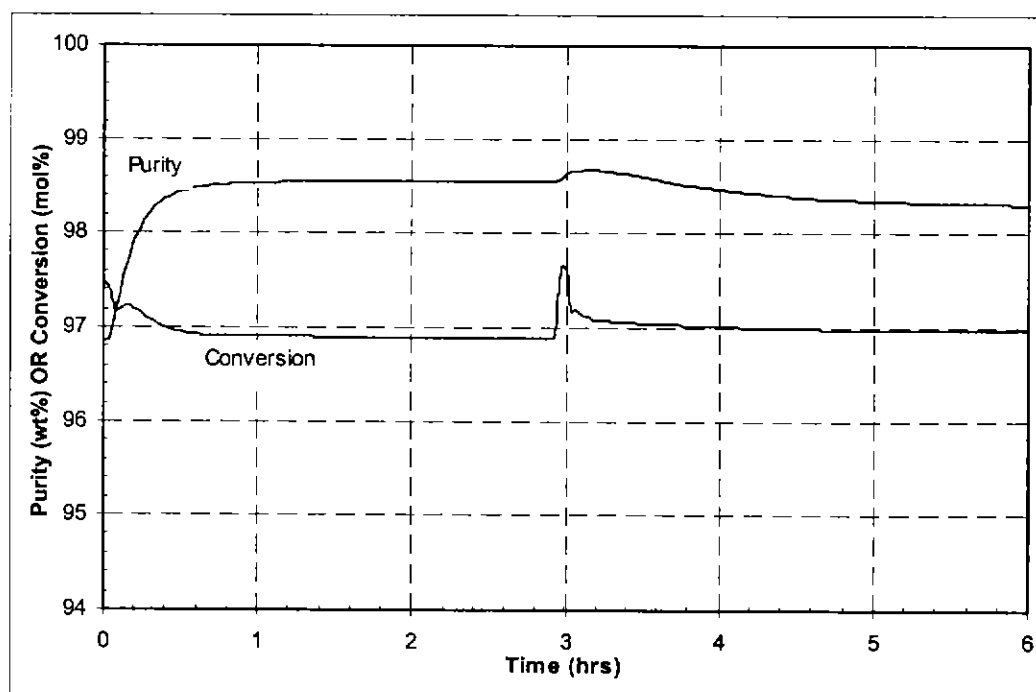


Figure 10.19 - Open-Loop Response to Composition Disturbances (Performance Test 2)

Interestingly, the feed rate disturbance has a larger effect on the system than the feed composition change. The LV control configuration is often favoured for non-reactive distillation *because* it provides good open-loop disturbance rejection of feed rate disturbances. This property arises as the feed rate usually affects fractionation only and not

the feed split. This is clearly not the case for reactive distillation and closed-loop control is required to counter feed rate disturbances (planned or otherwise).

Figures 10.18 and 10.19 demonstrate that open-loop control is inadequate for this column due to the large deviations from the initial conditions, thereby confirming earlier results (Section 9.3 and 10.2.1). Thus, the need for closed-loop control is established but the effectiveness of the three control modes proposed above must be evaluated against these open-loop responses (using performance tests 1 and 2 for consistency). Only substantially better disturbance rejection should be considered adequate, and set-point sensitivity (performance test 3) must be introduced as an additional requirement.

Each control mode was independently evaluated by subjecting the controller combination (per Table 10.5) to the relevant performance tests using dynamic simulations. The LV control configuration was used in each case to provide a consistent reference. The simulation results are presented below in Figures 10.20-10.27. The comparison with open-loop operation is favourable. Although the key process parameters are not being controlled directly (due to the measurement and control difficulties described previously), the control responses indicate that satisfactory to excellent control is possible in each mode. In all cases, the disturbances result in some deviation from the initial values of ETBE purity and isobutene conversion but the changes are generally not appreciable.

Control mode 1 is a two-point control scheme and the interactions between the two loops are clearly evident (especially in Figures 10.20 and 10.22). This reduces the ability of the controller to reach steady-state quickly. However, both the ETBE purity and reactant conversion are maintained close to their original values following feed rate and feed composition disturbances. Figure 10.21 indicates that the composition affects the temperature set-point required to produce a given value of purity and the set-point might need to be manually updated to control the purity tightly. This cannot be done automatically (via a cascade loop using an analyser signal or otherwise) as such a loop would only be stable over a narrow range of operating conditions. The process gain changes sign so that it is not immediately evident whether the master controller in the cascade system should increase or decrease the set-point of the slave controller in order to achieve a particular ether purity.

The set-point responsiveness of this control mode is compromised by the strong control loop interactions which exist between the purity loop (controlling a mid-stripping section temperature) and the conversion loop (controlling the reaction zone temperature difference).



However, Figure 10.22 shows that set-point changes can be implemented without destabilising the process, although the process settling time is significant (greater than two hours).

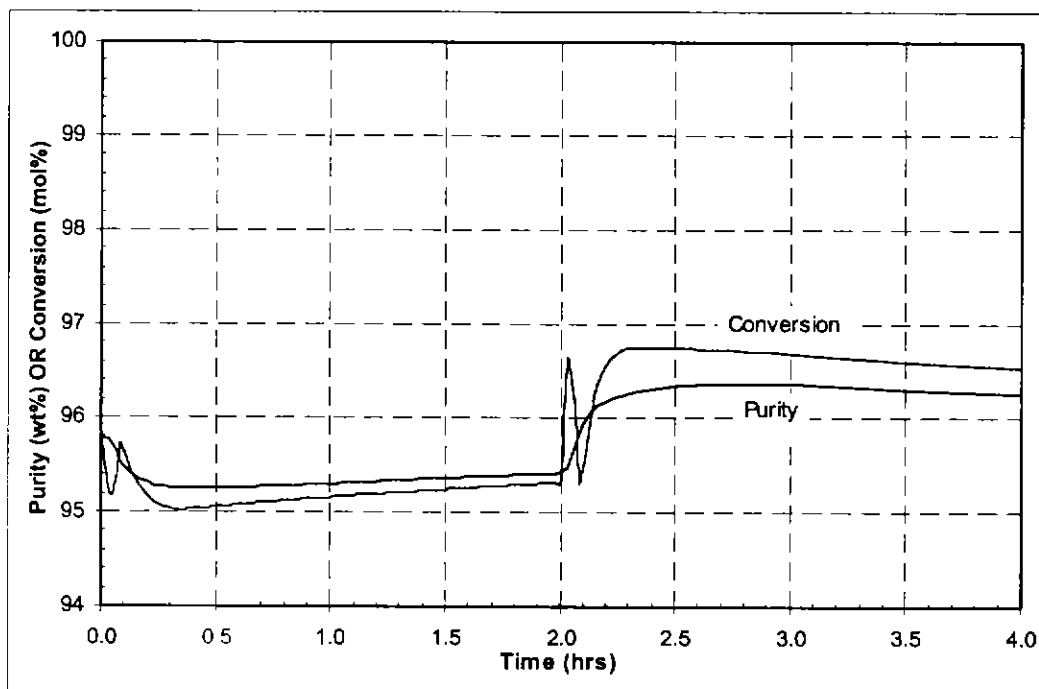


Figure 10.20 - Closed-Loop Response to Feed Rate Disturbances in Control Mode 1

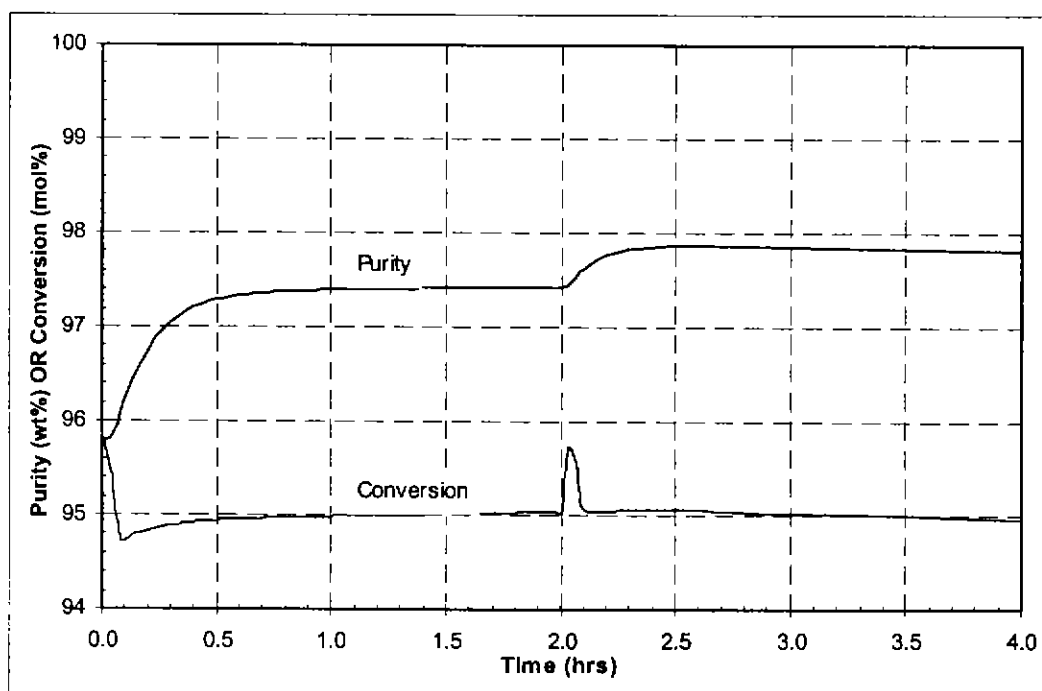


Figure 10.21 - Closed-Loop Response to Feed Composition Disturbances in Control Mode 1

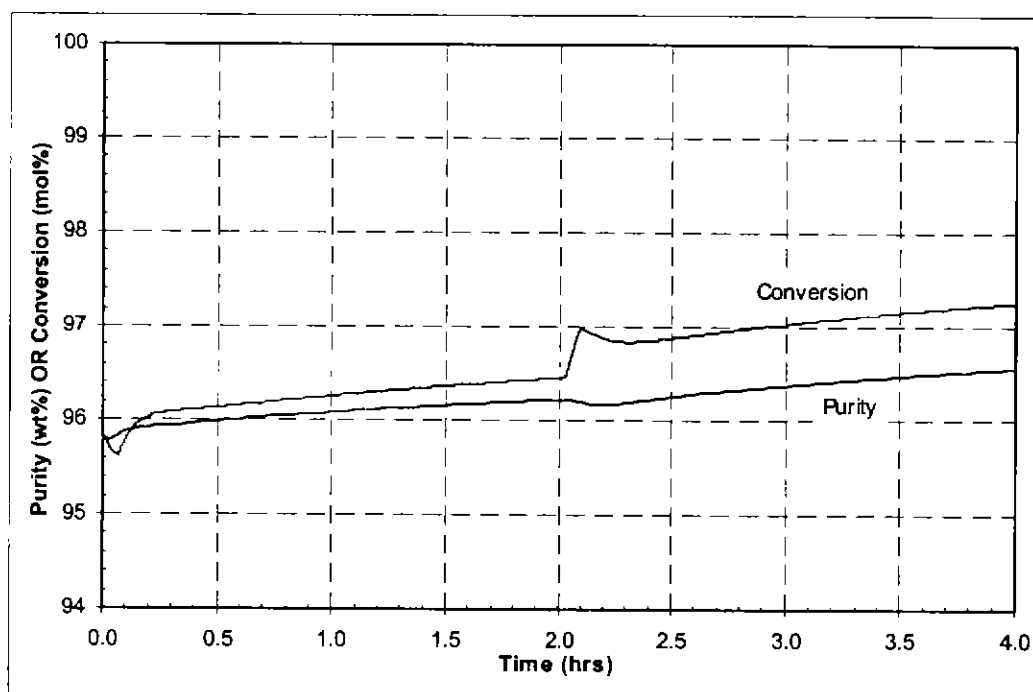


Figure 10.22 - Closed-Loop Response to Set-Point Changes in Control Mode 1

Control mode 2 is a simpler control structure that offers faster dynamic responsiveness than mode 1. The reflux rate is maximised to equipment constraints, which removes the control loop interactions in maximising the isobutene conversion for the target ETBE purity. The purity is maintained close to the original value for feed rate disturbances (Figure 10.23) but allows some variation for feed composition disturbances (Figure 10.24). As with control mode 1, manual adjustment of the temperature set-point could be required to keep the ETBE purity at a target value at all times. Only one set-point is used and Figure 10.25 shows that the controlled variable responds quickly to changes in its value. However, its steady-state sensitivity is very high so that relatively large changes are required to produce a substantive change in the desired process objective. In using the complete, integrated control scheme, it is important to realise that this sensitivity changes between modes (i.e. depending on whether the secondary control loop is in the manual or automatic condition).

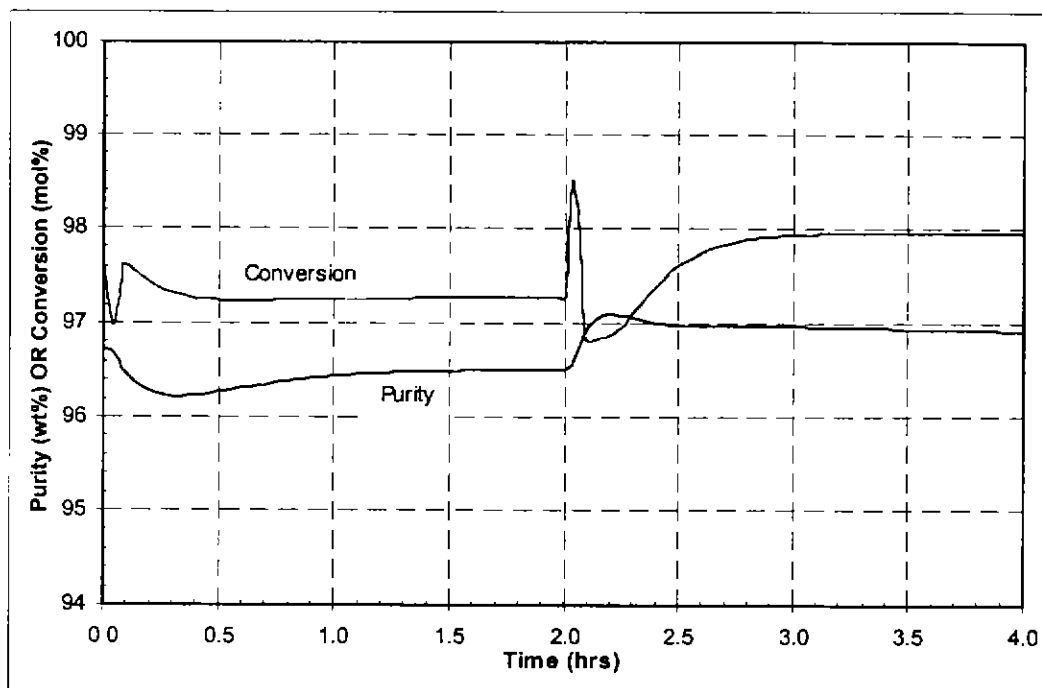


Figure 10.23 - Closed-Loop Response to Feed Rate Disturbances in Control Mode 2

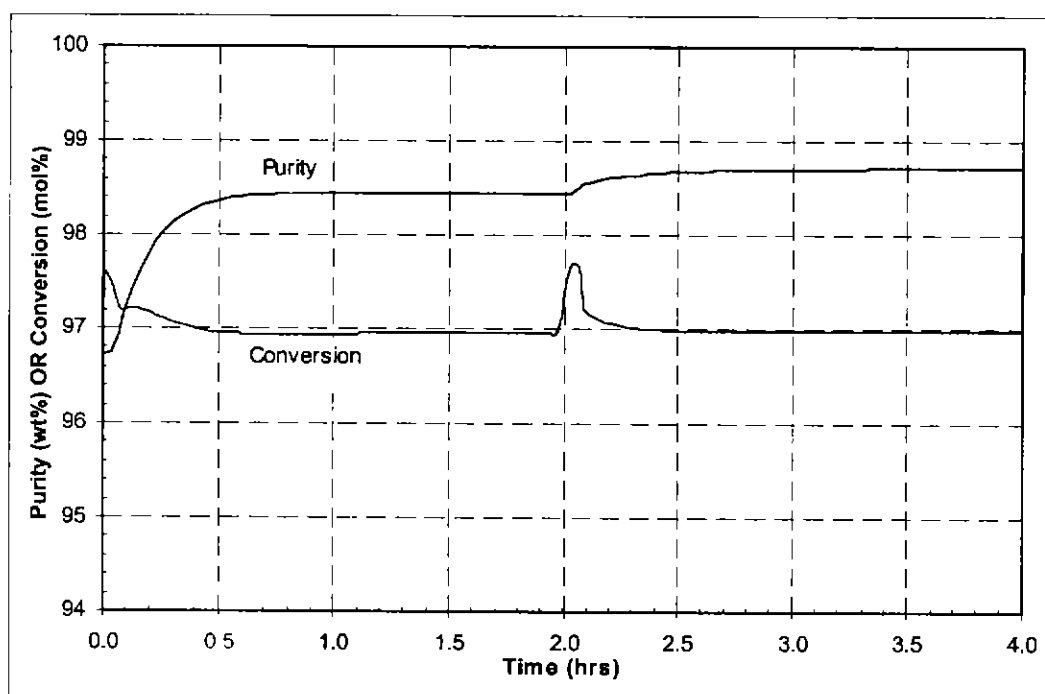


Figure 10.24 - Closed-Loop Response to Feed Composition Disturbance in Control Mode 2

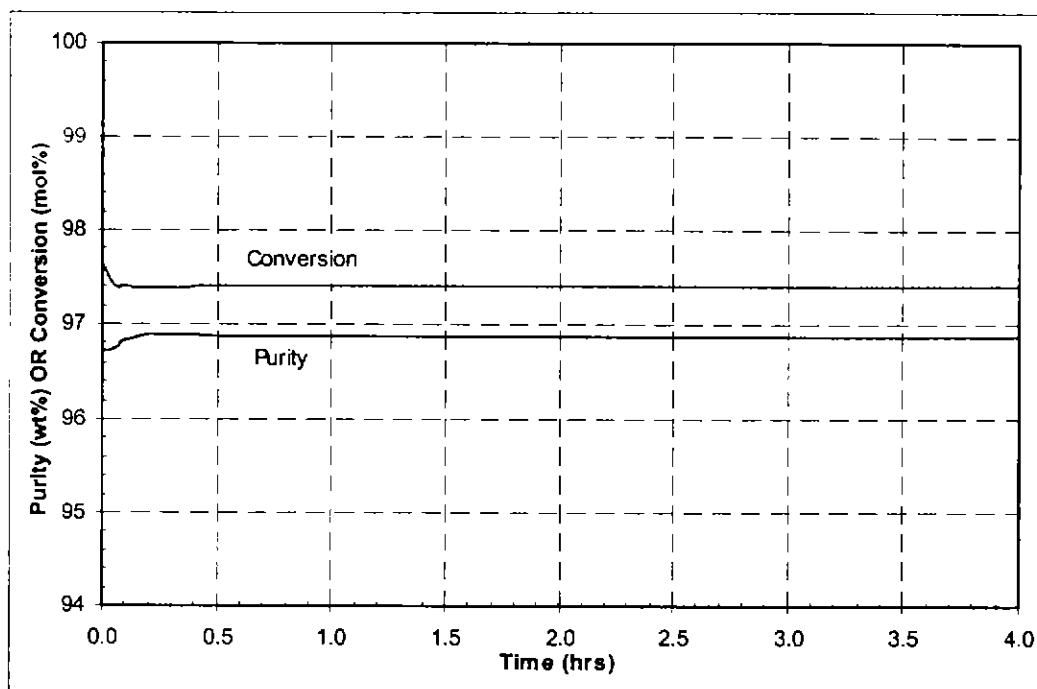


Figure 10.25 - Closed-Loop Response to Set-Point Changes in Control Mode 2

Only two responses are shown to characterise control mode 3 as no set-points are used directly in the control of the process so that set-point responsiveness is not a consideration. Figure 10.26 shows that the fluctuations following a feed rate change are larger than for the other modes but that the ETBE purity stabilises to a higher value after each perturbation. Although the isobutene conversion is maximised in this mode (by maintaining the reflux rate at its maximum value), the final values of the conversion are lower than in control mode 2.

This attribute of the control system is unavoidable as the optimum reboiler duty with respect to purity and the optimum with respect to conversion do not coincide exactly. Near the operating point for maximum purity, the conversion may decrease slightly following some disturbances. In other cases, both the conversion and purity will increase together. This property is not an indication of any inadequacy in the control structure but reflects the achievable process results and the control priorities (i.e. the first control objective, maximum purity, takes precedence over the second objective, maximum conversion). The comparison between Figures 10.24 and 10.27 is similar to Figures 10.23 and 10.26. The final ETBE purity is higher after each composition perturbation but the conversion is decreased slightly in each case.

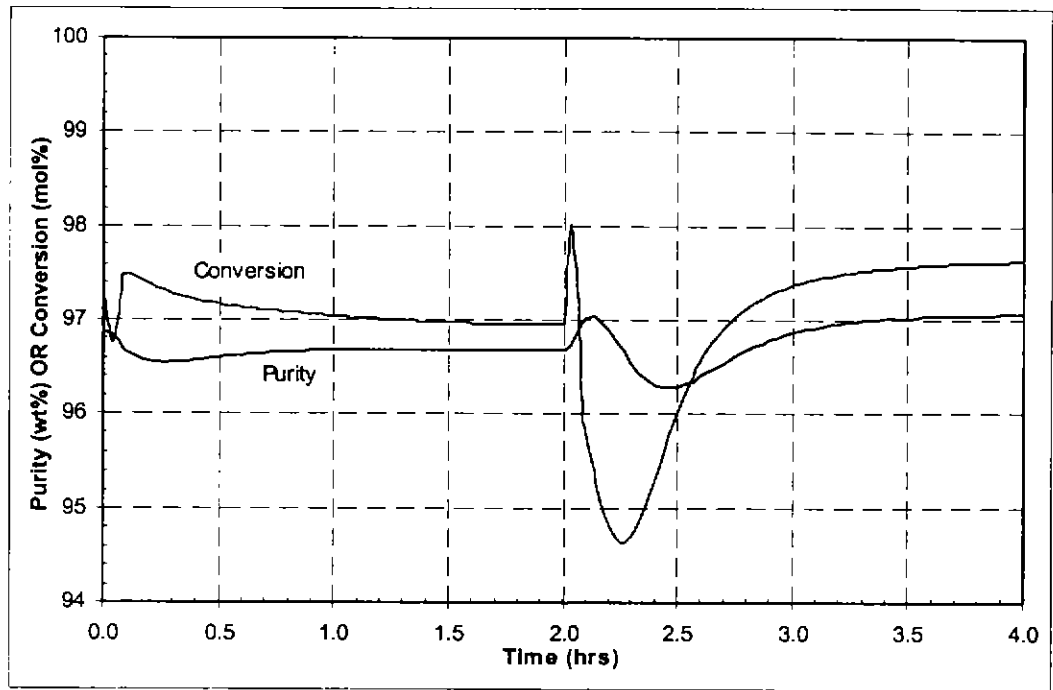


Figure 10.26 - Closed-Loop Response to Feed Rate Disturbances in Control Mode 3

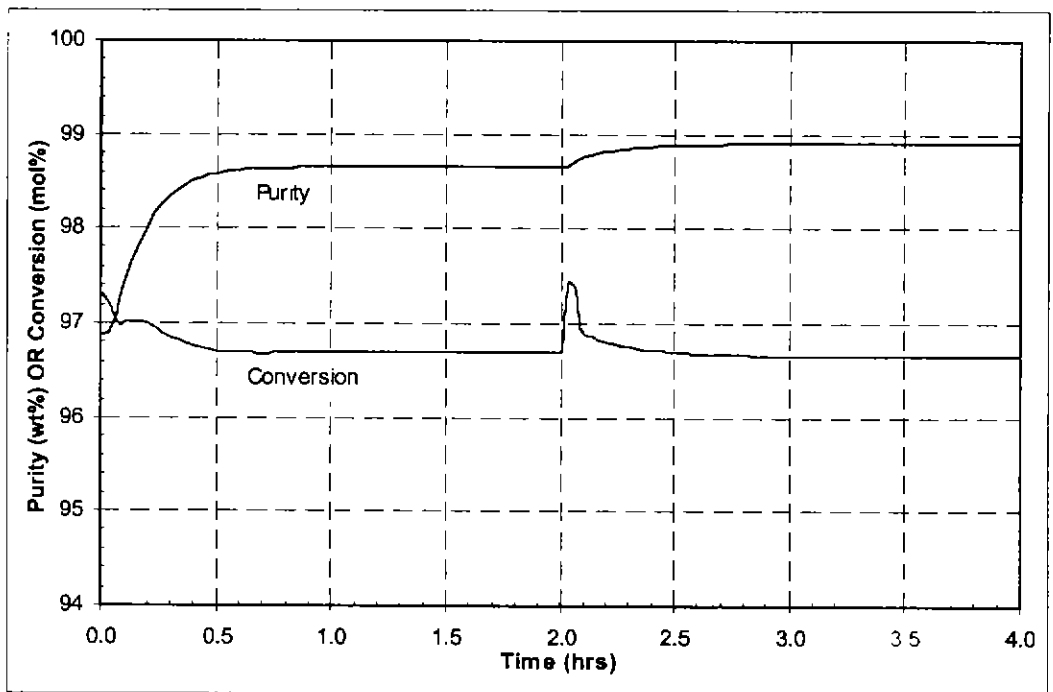


Figure 10.27 - Closed-Loop Response to Feed Composition Disturbances in Control Mode 3

### 10.3.5 Effectiveness of the Integrated Control Scheme

Dynamic simulations suggest that the three control modes are each stable for a wide range of process disturbances despite the cogent process non-linearity and bidirectionality. Thus, the proposed integrated control scheme allows for the column operation to adequately reflect a changing economic environment that could require the process objectives to be regularly revised.

The control objectives were derived from the process objectives in a manner which maximised the process linearity and provided effective control loops, and the resulting control structure was shown to be capable of maintaining the process objectives within acceptable limits following perturbations in the feed rate and composition. Although accurate regulatory control of neither the ETBE product purity nor the reactant conversion was achieved (primarily due to measurement difficulties and the process bidirectionality), a mechanism was provided to manually increase or decrease the desired qualities.

Control mode 1 provided control of both the ETBE purity and the isobutene conversion via two composition control loops. Strong loop interactions were predicted by the high RGA values and this reduced the dynamic responsiveness of the control system. However, key process disturbances were suitably rejected by the controller and the process could be manipulated satisfactorily via the available set-points. The second control mode maximised the reactant conversion while retaining control of the purity. This was achieved by operating the reflux control loop in manual (at a value near the equipment constraints) and resulted in a much more responsive control system as the loop interactions were eliminated. Control mode 3 successfully maximised both the ETBE purity and the conversion, although purity loop was given a higher priority. This had a slightly detrimental effect on the conversion that was achieved because the operating point for maximum purity and maximum conversion do not coincide exactly. Process fluctuations also increased since the purity set-point was automatically adjusted with feed rate changes. However, the controller meets the process objectives.

At this point (i.e. after a satisfactory regulatory control system has been implemented), more advanced control applications can be considered to further improve the control performance. The process is a good candidate for multivariable predictive controllers (e.g. dynamic matrix control) as the control objectives can be changed continuously according to an overall economic optimisation. This type of controller also allows process constraints to be directly incorporated into the control scheme and can be extended to provide optimisation for interacting process units. However, the process bidirectionality must be considered at

all times as the poor selection of control loops and variable pairings could easily result in an unstable controller.

It is important to realise that the effectiveness of the MPC is directly related to the effectiveness of the underlying linear control system which itself is strongly influenced by the choice of controlled and manipulated variables and the control structure. MPC is not effective for systems with: order of magnitude changes in process gains; sign changes in process gains; and highly unusual step responses. Reactive distillation commonly displays all of these attributes so that the performance of a MPC could be severely retarded by poor implementation. MPC is becoming increasingly common in the oil and gas industries so that it is often regarded as a panacea for all control problems. It is not! Often, comparable performance is achievable with well designed and well tuned PI controllers.

## **10.4 OVERALL SUMMARY OF FINDINGS ON PROCESS DYNAMICS AND CONTROL ISSUES**

Steady state simulations of hybrid reactive distillation provided new and valuable information for the design and optimisation of processes for ETBE and MTBE synthesis (Chapters 3-6). However, dynamic simulations are required to adequately investigate process dynamics and control issues. These areas are of interest due to the complexity and novelty of reactive distillation and the implications of poor operability and controllability: the steady state benefits will not be realised unless satisfactory and consistent operation near the design point is possible. Chapters 7-10 present a range of discussions and investigations that address this fundamental issue.

It was shown that the steady state reactive distillation model could be extended to the dynamic case if appropriate additions and modifications were made to the equation structure. The dynamic model must be fully closed and complete to prevent index problems arising in the numerical solution of the set of differential and algebraic equations. However, acceptable models were developed to incorporate reaction kinetics or by assuming chemical equilibrium. The dynamic model was initially used to predict the open-loop responses to a range of operating disturbances, and then to examine transient responses to parametric changes in the model (e.g. the catalyst activity and the heat transfer rate in the condenser).

A combination of steady state and dynamic simulations were used to investigate multiplicity in hybrid reactive distillation. It was concluded that input multiplicity would be present in

all hybrid columns for ETBE or MTBE synthesis due to the VLE behaviour of these systems and the duality of effects that influence the reaction rate. Output multiplicity was also found in some columns and it was shown that physically realisable multiplicities are possible because of: (a) unit singularities; (b) the influence of the energy balance; (c) azeotropes; and (d) reaction hysteresis. Some output multiplicities (including several well known reports from the literature) were classified as pseudo-multiplicity since they were only possible if the system was constrained unrealisably (e.g. a constant molar flow). Where multiple steady states exist, it was found that all steady states are accessible since transitions between parallel steady states could be initiated by perturbations in either manipulated or disturbance variables. This behaviour has implications for equipment selection and start-up procedures, and also influences the control strategy.

Manual (open-loop) control of reactive distillation was found to be essentially infeasible due to the precision required and the capability of the process to shift between parallel steady states. One-point control can be effective and offers advantages where equipment constraints are important. However, care is required in selecting a controlled variable in order to avoid very non-linear and non-monotonic behaviour. Dynamic simulations were used to assess a range of control structures for their applicability for ETBE reactive distillation and the LV and the LB configurations were found to provide the best disturbance rejection and set-point sensitivity under a range of conditions.

The complexity of the reactive distillation process presents challenges for two-point control due to the range of interactions and non-linear responses that are present. However, several control strategies were developed and tested via dynamic simulations to determine a suitable approach. An inferential conversion controller was found to be effective in providing control of the reaction and could be implemented in conjunction with composition control using one of the schemes tested for one-point control. An integrated control scheme was also developed to provide for changing economic circumstances that affect the control objectives. Overall, the LV control structure was found to yield the best combination of control performance and stability for columns that can exhibit multiple steady states. The inventory control problem is simplified with this approach and appropriate control applications can be implemented to manage unwanted transitions between parallel steady states.



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## CHAPTER ELEVEN

### EXPERIMENTAL EQUIPMENT

- 11.1 Pilot Plant Objectives**
- 11.2 Design Basis and Expected Operating Conditions**
  - 11.2.1 Design Basis
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- 11.3 Reactive Distillation Column**
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  - 11.3.2 Separation Section Packings
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  - 11.4.2 Bottoms Cooler
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  - 11.5.1 Hydrocarbon Feed Storage
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- 11.6 Instrumentation**
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  - 11.6.4 Level Indicator and Transmitter
- 11.7 Control System**
- 11.8 Installation in the Laboratory**
- 11.9 Costs**

#### 11.1 PILOT PLANT OBJECTIVES

A reactive distillation pilot plant was constructed to synthesise ETBE from a hydrocarbon stream containing isobutene and ethanol in order to support the simulation studies presented in Chapters 3-10. The motivation and long-term objectives for the experimental investigation are as follows:

- confirm the applicability of reactive distillation technology for ETBE production;
- validate steady state and dynamic simulation results obtained from Pro/II (Simulation Sciences, 1994) and SpeedUp™ (Aspen Technology, 1993);

- demonstrate that ETBE can be produced in the industrially significant range of isobutene conversions and product purities from a locally sourced hydrocarbon feed;
- implement a range of novel advanced control schemes designed specifically for reactive distillation columns;
- demonstrate the phenomena of multiplicity and hysteresis for reactive distillation columns synthesising ETBE;
- test a range of novel packings for conventional fractionation and reactive distillation in pilot scale columns;

The pilot plant equipment will also provide a means to:

- assess the economic viability of the reactive distillation process based on future demand for local ether production;
- assess the effectiveness of the reactive distillation design techniques which were proposed in Chapter 5;
- investigate operability issues associated with start-up and steady state operation of a reactive distillation column;
- determine the maximum isobutene conversion and ether product purity which can be obtained from the experimental equipment and, therefore, to develop relationships between design parameters and performance.

## 11.2 DESIGN BASIS AND EXPECTED OPERATING CONDITIONS

### 11.2.1 Design Basis

The pilot plant was originally designed for a feed that duplicates industrial conditions: a pre-reacted mixture of  $C_4$  hydrocarbon, ethanol and ETBE (see Chapter 6). Specifically, the source hydrocarbon was assumed to contain 40% isobutene (i.e. typical of a steam cracking unit: Parra et al., 1994), a stoichiometric excess of 5.0% ethanol was nominated and the upstream reactor was assumed to operate at an outlet temperature which provided 80% isobutene conversion. The design feed rate was selected based on flooding estimates for typical small-scale packings and a column internal diameter of 155 mm. Column operation was simulated and optimised on both Pro/II and SpeedUp in order to maximise isobutene conversion without compromising the ETBE product purity. Table 11.1 indicates the design basis, the predicted results and the expected operating conditions.

The design basis compares favourably with reactive distillation equipment described in the recent literature. Two columns are being actively used at present for pilot scale synthesis of ethers: (a) in Finland, Neste have a column at Abo Akademi, which they have used to

produce TAME but at a conversion of only around 30% (Bravo et al., 1995); and, (b) in Germany, Technische Universität Clausthal have a bench-top column (1600 mm x 53 mm i.d.) without a rectification section, which they have used to produce MTBE (Flato and Hoffman, 1992) and demonstrate oscillatory behaviour (Sundmacher and Hoffman, 1995).

**Table 11.1 - Original Design Basis**

<b>Feed Conditions</b>	
Feed rate	760 ml/min
Feed composition (wt%)	6.1% ethanol, 6.0% isobutene, 43.3% ETBE, 44.6% n-butene
<b>Product Specification</b>	
Bottoms product rate	380 ml/min (50% vol. yield)
Overhead product rate	370 ml/min (49% vol. yield)
Distillate composition (wt%)	98.2% n-butene, 1.0% ethanol, 0.8% isobutene, 0.1% ETBE
Bottoms composition (wt%)	96.1% ETBE, 2.0% ethanol, 1.8% butenes, 0.1% DIB
Isobutene conversion	98.5 mol%
<b>Operating Conditions (Simulation Data)</b>	
Overhead pressure	950 kPag
Condenser duty	6.7 kW
Reflux rate	1850 ml/min
Reflux ratio	5.0
Reboiler duty	9.1 kW (including heat losses of 1.0 kW)
Condenser outlet temperature (T1)	40°C
Overhead temperature (T2)	74°C
Temperature above reaction section (T3)	75°C
Temperature above stripping section (T4)	90°C
Temperature mid-stripping section (T5)	127°C
Bottoms temperature (T6)	159°C

### 11.2.2 Hydrocarbon Feed from Kwinana Refinery

In May 1996, BP Oil Australia agreed to supply hydrocarbon from the feed to the alkylation unit at Kwinana Refinery (immediately downstream of the catalytic cracking unit) for use in the pilot plant. The composition of the sample (approximately 80 L; taken on 2nd May, 1996) which was provided is shown in Table 11.2 and is considered typical for this source. However, the crude type, the processing conditions and the product slate will all affect the composition of this stream and key quantities (e.g. the isobutene concentration and the total C<sub>3</sub> concentration, etc.) can be expected to vary somewhat if another sample is taken in the future.

Table 11.2 - Measured Composition of Hydrocarbon from Kwinana Refinery

Component	mol%
Isobutene	12.5
1-Butene	11.5
trans-2-Butene	12.8
cis-2-Butene	7.9
Butadiene	0.3
Isobutane	30.4
n-Butane	23.4
Propane	0.8
Propene	0.4
Total	100.0

Two simulation cases were evaluated with the feed composition given above: (a) raw feed plus 5.0% excess ethanol at an overhead pressure of 950 kPag, reflux ratio of 5.0 and reboiler duty optimised with respect to isobutene conversion and the ETBE purity; and, (b) pre-reacted feed (80% isobutene conversion to ETBE) with the same conditions as used for case (a). The results are summarised in Table 11.3. The relatively low concentration of isobutene in the hydrocarbon from Kwinana Refinery (compared with the original design basis) generally reduced the attainable performance. Compared with the simulation data shown in Table 11.1, the maximum conversion is lower, the corresponding ETBE product purity is lower, and the volumetric yield of the ETBE product was substantially lower when the Kwinana Refinery sample was used.

The capacity of the pilot plant column was also reduced by the relatively higher energy requirement (since more inerts must be recovered overhead) and the design feed rate was reduced to 450-500 ml/min. The other operating conditions remain similar to the original

design basis but a more extensive optimisation of operating pressure, reflux ratio and reboiler duty (to be undertaken during experimental testing) might result in some changes to the expected operating conditions which are indicated in Table 11.1. Interestingly, there is virtually no difference between cases (a) and (b). This indicates that, in an industrial application, a pre-reactor is essentially only required for convenience and could be eliminated if an appropriate means of regenerating the catalysts *in situ* was found.

**Table 11.3 - Predicted Pilot Plant Results with Kwinana Refinery Feed**

	<b>Case (a)</b>	<b>Case (b)</b>
<i>Operating Conditions</i>		
Isobutene conversion (mol%)	93.4%	95.6%
Bottoms composition (wt%)	93.0% ETBE, 0.4% ethanol, 0.2% DIB, 6.4% hydrocarbons	93.0% ETBE, 0.4% ethanol, 0.2% DIB, 6.4% hydrocarbons
Distillate composition (wt%)	0.1% ETBE, 1.2% ethanol, 98.7% hydrocarbons	0.1% ETBE, 1.2% ethanol, 98.7% hydrocarbons
<i>Volumetric Yields</i>		
Bottoms product	17%	17%
Distillate product	82%	83%
<i>Temperature Profile</i>		
Condenser outlet temperature (T1)	40°C	40°C
Overhead temperature (T2)	74°C	74°C
Temperature above reactive section (T3)	77°C	77°C
Temperature above stripping section (T4)	80°C	81°C
Temperature mid-stripping section (T5)	104°C	114°C
Bottoms temperature (T6)	155°C	160°C

## 11.3 REACTIVE DISTILLATION COLUMN

### 11.3.1 Mechanical Design of Column

The mechanical design of the column was completed to AS1210 (Australian pressure vessel code) requirements. The wall thickness of a standard 150 mm schedule 40 stainless steel (grade 316) pipe was sufficient for the operating pressures required. The shell was constructed in five pieces to allow the packings and the catalyst to be installed and removed as required. Flat ends were specified to simplify construction. The individual shell sections and ends were all flanged together and sealed with o-rings. Table 11.4 indicates critical dimensions and thicknesses.

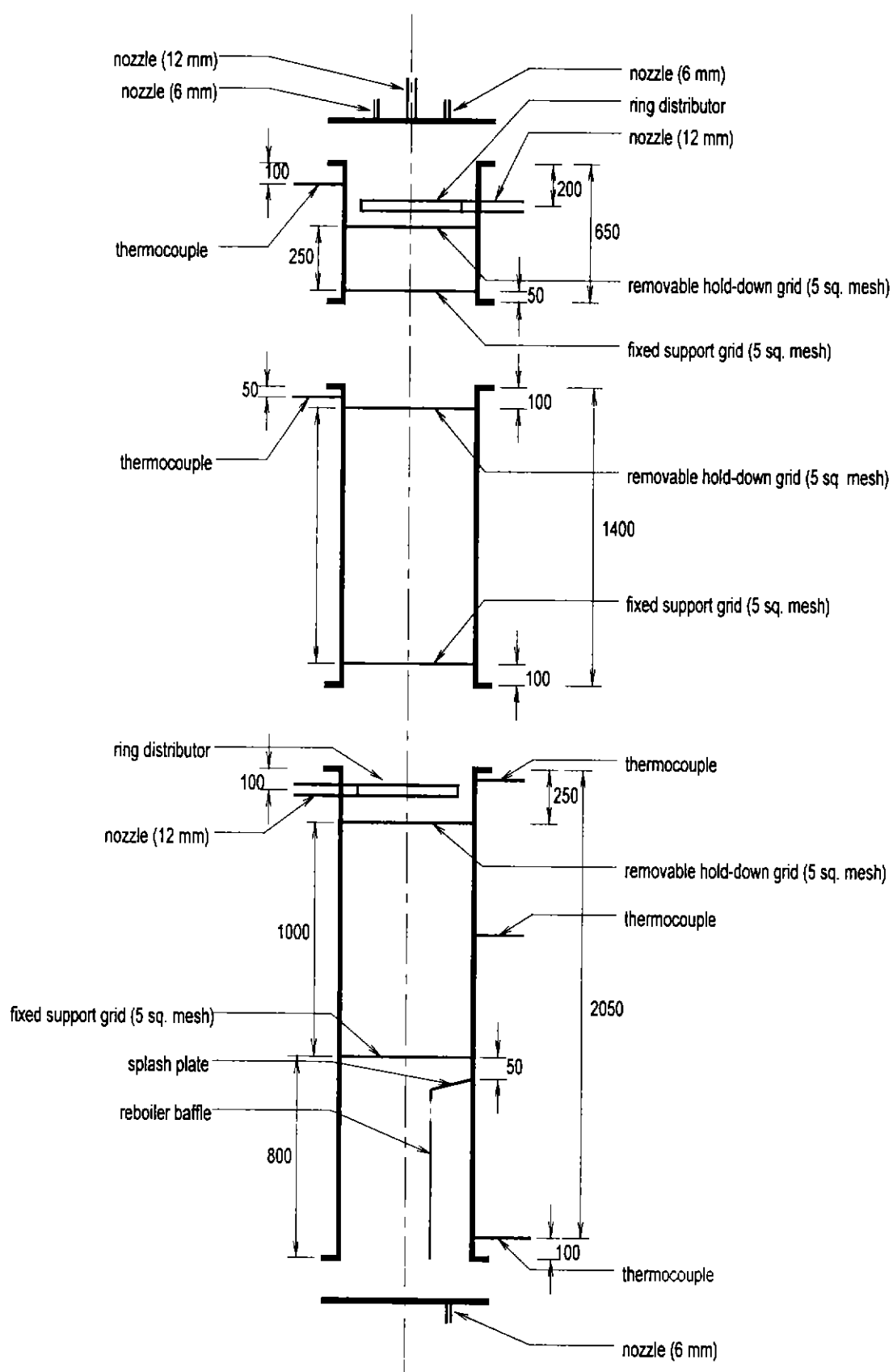
Table 11.4 - Mechanical Column Design

	Minimum Required	Actual Specified
Wall thickness (mm)	4	7
End thickness (mm)	12	20
Flange thickness (mm)	11	20
Bolts (mm)	8	12

The nozzles, connections and internals are depicted in Figure 11.1. Both feed nozzles are removable, as are all the thermocouples. A pressure relief valve (PRV) discharges from the top of the column back to the main feed tank. The feed tank vents outside the laboratory to the atmosphere. The top end plate also contains a lifting ring in its centre to support the column during installation and operation. The end plates contain the necessary discharge nozzles for the distillate and bottoms products.

### 11.3.2 Separation Section Packings

A novel structured packing design was developed for this column. Sheets of expanded metal with appropriate openings (6 mm x 3.5 mm) were cut into strips (300 mm wide) and rolled into cylinders that fitted snugly inside the column. The rolled cylinders provided a substantial contact area and a complicated flow path, which suggests an adequate HETP. Air-water tests indicated that these packings also provide adequate capacity, holdup and radial dispersion and a low pressure drop. It was not possible to rigourously test these packings in a distillation environment before the column was built, but the significant cost saving compared with commercial packings (e.g. \$334/L for 6 mm raschring rings compared with \$16/L, excluding labour, for the rolled cylinders) provided the incentive to pursue the more novel (and therefore riskier) approach.



**Figure 11.1 - Reactive Distillation Column Design**



The structured packings were installed in the column on a support grid constructed from 5 mm x 5 mm stainless steel mesh mounted on a ring welded inside the column. A similar hold down grid was also manufactured and can be secured at the top of the packed bed to prevent movement of the packing due to rapidly expanding vapour. However, the weight of the packing (2.05 kg/L), which would be a disadvantage for commercial installations, is sufficient to prevent internal movement in this case.

### 11.3.3 Reactive Section Packings

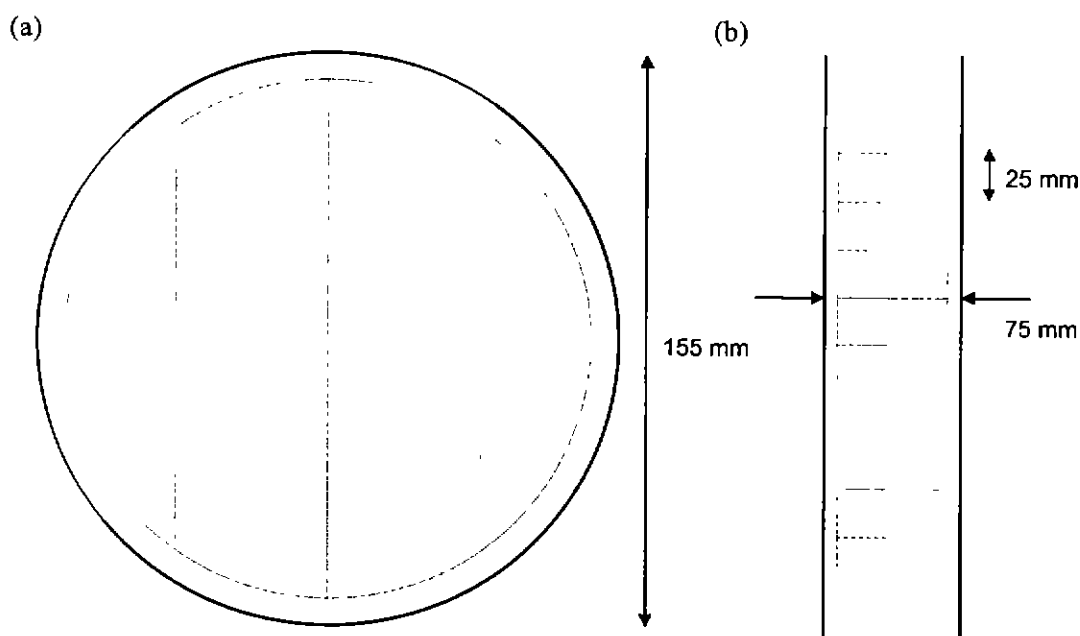
The reactive section was required to accommodate packings for mass transfer and sufficient catalyst for the ETBE reaction to approach chemical equilibrium. Several commercial cation exchange resins are suitable to catalyse etherification reactions and Amberlyst 15™ was used based on availability and cost. SpeedUp simulations incorporating a full kinetic model of the reaction (Chapter 3, Section 3.2) indicated that the isobutene conversion would be within 0.1% of the equilibrium conversion and that the variation in stage-to-stage reaction rates would be acceptable if a total of 11.5 kg of catalyst was used. This is equivalent to 2.5 L of catalyst at a bulk density of 0.61 g/cm<sup>3</sup> (Zhang and Datta, 1995).

The catalyst has a mean particle size of approximately 0.7 mm (Zhang and Datta, 1995) and is, therefore, too small to be packed directly in the column because of hydraulic restrictions alone. A suitable catalyst packing arrangement was, therefore, required to provide adequate contact between liquid and catalyst to allow the reaction to progress normally and adequate vapour space to prevent flooding. Several packing arrangements were tested using cloth to contain the catalyst particles. The packing arrangements tested fall into two categories: (a) arrangements based on circular sachets of catalyst (Figure 11.2a); and, (b) arrangements based on rolled cloth strips containing catalyst (Figure 11.2b). Three types of material were tested: (a) interfacing; (b) 'Chux' wipes; and, (c) fine terylene weave (a lightweight curtain material). The materials were chosen to offer minimal resistance to both liquid and vapour but provide adequate strength to prevent tearing. Of the materials investigated, interfacing had the greatest strength and workability while the nylon mesh offered least resistance to flow.

Tests were performed on the various catalyst packing arrangements using the same packed column rig that was used to test the separation section packings. Graded sand (0.50-0.85 mm) was initially used in place of the catalyst. The catalyst sachets were tested with 40 ml of graded sand (full) and 20 ml of graded sand (half-full) per sachet. However, none of the test materials provided adequate capacity for the proposed operating conditions, either when full or half-full, and severe flooding was experienced at low liquid and vapour

loadings. Catalyst bales, constructed to the dimensions given in Figure 11.2b, and filled with approximately 4 ml of graded sand per pocket were also tested. A relatively high pressure drop was observed but flooding was not detected at the proposed vapour and liquid flows. The test results were corrected for differences in physical properties between the air-water system and the hydrocarbon mixture using the generalised pressure drop correlation (GPDC) for packings (Kister, 1992). On this basis, it was considered that flooding was still possible in the pilot plant for the proposed operating conditions, and a second catalyst bale was constructed using a 50 mm strip of mesh interleaved with the catalyst bale. This arrangement had a significantly lower pressure drop and, based on the GPDC, is considered unlikely to flood at the operating conditions expected in the pilot plant column.

Six catalyst bales (two per reactive stage) were constructed using the cloth strip design, shown in Figure 11.2b, interleaved with 2.4 m of 50 mm mesh strip. Each roll contained approximately 160 pockets so that the total volume of catalyst in the reactive bed (three stages) was approximately 4.0 L. This is equivalent to around 2.4 kg of catalyst and should be sufficient to ensure that the reaction progresses close to equilibrium. The overall structure of the reactive bed consisted of catalyst rolls interspersed with randomly packed pieces of expanded metal (approximately 25 mm x 25 mm) of the same grade used in the separation section beds. A greater packed height per stage was used in the reactive section as the configuration specified was estimated to have a higher HETP.



**Figure 11.2 - Catalytic Packing Design: (a) Catalyst Sachet; (b) Catalyst Bale**

As with the stripping and rectifying sections, a support grid and hold down grid were manufactured. The support grid was welded to a ring which was welded inside the column while the hold down grid attached to another ring welded into the column in order to prevent disruption of the packed bed.

#### 11.3.4 Distributors

Lateral mixing is usually sufficient to eliminate the need for liquid distributors if the ratio of the column diameter to packing diameter ( $D/d_p$ ) is less than 20 (Kister, 1994). Most pilot scale columns meet this criterion as the packing size is usually large compared with the column diameter. However, structured packing is more sensitive to maldistribution and the design of the separation section packings is susceptible to channelling so that the use of distributors might be beneficial.

A ring distributor was selected for the feed. A drip point analysis (Kister, 1994), Figure 11.3, suggested that a six point distributor would produce the most consistent liquid distribution without leaving the centre dry. The ring diameter was selected to provide adequate flow at the walls using the empirically derived formula shown in equation (11.1).

$$D_r = D \cdot \left( 1 - \frac{1}{\sqrt{N}} \right) \quad (11.1)$$

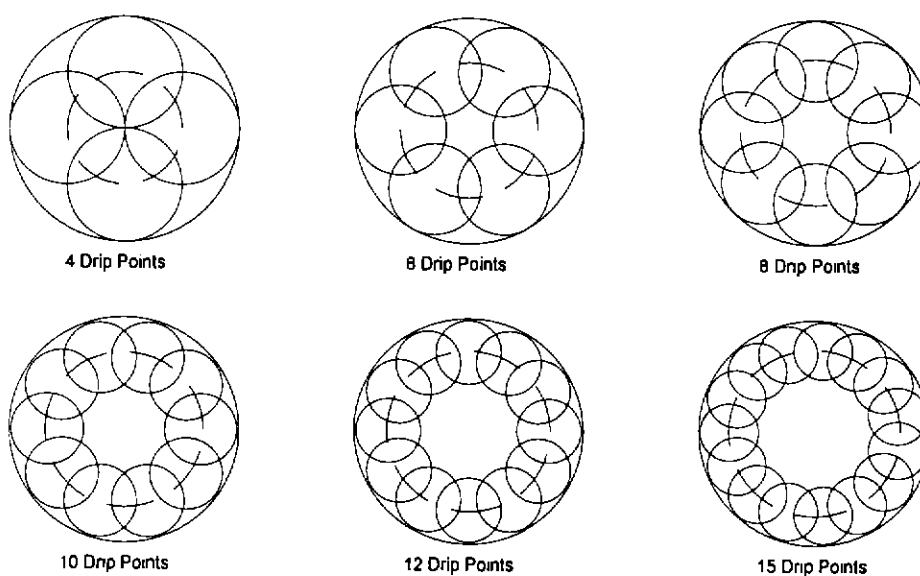
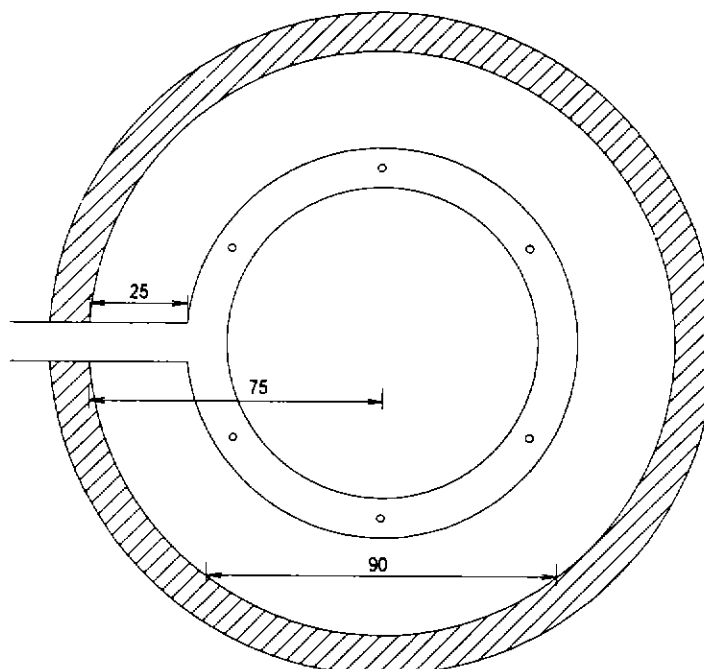


Figure 11.3 - Ring Distributor Designs

The diameter of the drip holes (1.0 mm i.d.) was selected to guarantee a large ratio of exit pressure drop to transport losses which is conducive to good distribution of liquid around

the distributor ring. The additional pressure drop created by the small hole diameter is compensated by surplus pump head. The distributor dimensions are shown in Figure 11.4.



**Figure 11.4 - Feed and Reflux Distributors**

The reflux distributor was based on the same basic design in order to provide good radial distribution. However, an identical design would have created an excessively large pressure drop within the reflux circuit that relies on gravity flow. Therefore, larger holes (3.0 mm i.d.) were specified.

### 11.3.5 Internal Reboiler

The predicted bottoms temperature at 950 kPag is around 160°C. This precludes the use of steam as a heating medium since a steam pressure of 1500-2000 kPa would be required to provide an adequate temperature difference. A lower operating pressure would allow steam to be used with a reduced pressure but the attainable performance would be compromised and additional catalyst would be required to compensate for the lower temperatures and, therefore, lower reaction rates.

An internal, direct contact, electric heating element was specified to provide the necessary boilup. This simplifies the construction of the column by eliminating the need for the separate reboiler vessel that would be required if a thermosiphon reboiler was used. Although the element will reach high temperatures (approximately 220°C), auto-ignition is unlikely in the oxygen deficient environment inside the column. The design duty for the

reboiler could only be met with stainless steel elements and a three phase power supply, requiring three separate elements to be manufactured. Each element was fixed to the base of the column and sealed to prevent leakage. A variable frequency drive (voltage regulator) and ammeter were connected in series with the elements to regulate the reboiler duty and measure the current draw (and, therefore, power supplied). A digital controller on the variable frequency drive allows the voltage to be specified exactly. The maximum rated duty of the installed elements is 7.5 kW.

Inside the column, a baffle separates the liquid being heated from the bottoms product to be removed. Weirs in the baffle ensure that the heating element is covered by liquid at all times and a splash plate connected to the top of the baffle ensures that all liquid coming from the packed bed enters the reboiler sump before leaving the column. This configuration is depicted in Figure 11.1.

#### 11.3.6 Insulation

Heat losses are typically significant for pilot scale distillation columns, especially where multiple flanges are used (Kruse et al., 1995), due to the relatively high ratio of surface area to internal volume. Insulation, to a thickness of 25-50 mm, was applied *in situ* to minimise the effect of heat losses on the column performance.

### 11.4 ANCILLARY EQUIPMENT

#### 11.4.1 Overhead Condenser

The overhead condenser was constructed as a double pipe exchanger with condensation in the inner pipe. Chilled water from the shared laboratory network was used as the cooling medium. The duty required at maximum reboiler duty (7.5 kW) was estimated to be 7.3 kW via simulations. This is attained at a cooling water flow of approximately 10 L/min with a chilled water temperature rise of 10°C.

The condenser configuration and dimensions are indicated in Figure 11.5. This results in a heat transfer area of 0.24 m<sup>2</sup> and an estimated heat transfer coefficient of 500-600 W/m<sup>2</sup>/°C (based on rigorous calculations). The condensing temperature is almost independent of the feed-split since the distillate vapour pressure is dominated by the effect of the C<sub>4</sub> components. At 950 kPag, the condensing temperature is approximately 74°C giving a LMTD of 51°C, and a duty of 7.3 kW. Thus, there is no surplus area at design conditions but the maximum chilled water flow is greater than 50 L/min and the LMTD can be increased by raising the pressure. Acceptable operation is also possible with a reduced

condenser duty if either the feed rate or the reboiler duty is lowered from the design basis. The pressure drops through both the inner and outer pipes are acceptable.

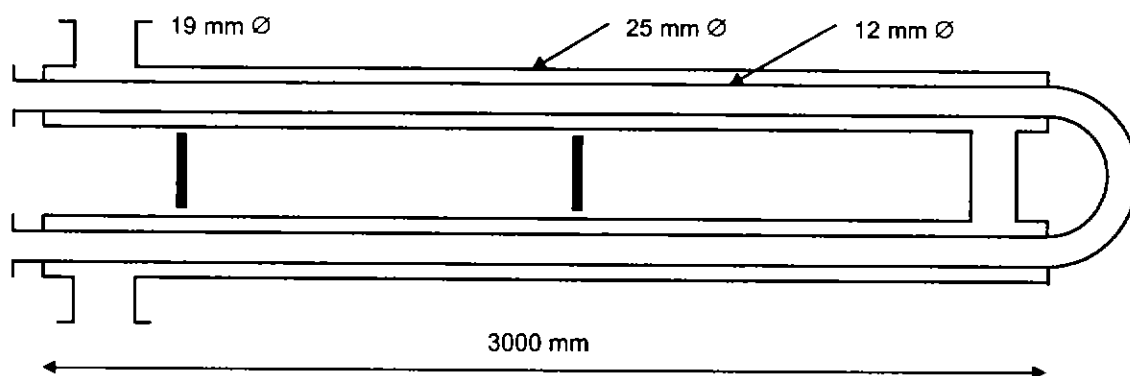


Figure 11.5 - Overhead Condenser

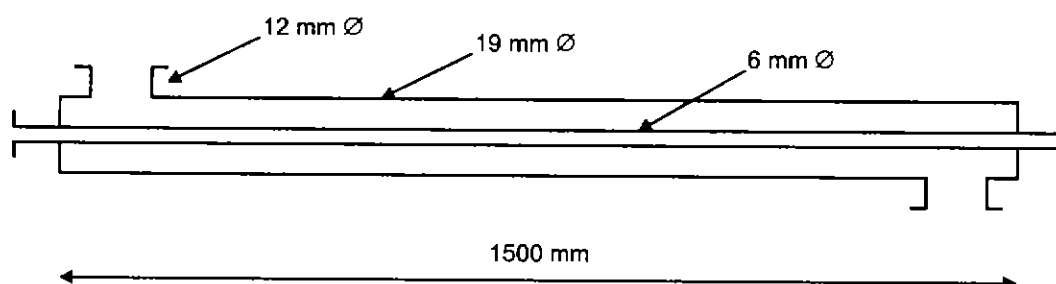


Figure 11.6 - Bottoms Cooler

The response of the system to inadequate cooling will be for the column pressure to rise until there is adequate temperature driving force for complete condensation. The outlet temperature will also rise and increase the pressure in the distillate storage cylinders. The pressure rating of these cylinders is more than adequate to handle any variation resulting from fluctuations in cooling. However, an increase in distillate pressure might endanger the instrumentation. Therefore, the column feed rate should always be reduced until pressure control is regained.

### 11.4.2 Bottoms Cooler

A second double pipe exchanger was installed to cool the bottoms product from an estimated 160°C to approximately 40°C to permit safe handling and easy storage. This equates to a duty of approximately 320 W. The laboratory chilled water was again utilised to provide the necessary cooling. The configuration and dimensions of the bottoms cooler are indicated in Figure 11.6 and are similar to the overhead condenser. The bottoms cooler is considerably shorter than the condenser since a much lower duty is required. A smaller diameter inner pipe was used to accommodate the lower flow rates (a 12 mm pipe would have resulted in sluggish flow and a poor heat transfer coefficient).

The heat transfer area was calculated to be 0.030 m<sup>2</sup>, the heat transfer coefficient for forced convection was estimated at 198 W/m<sup>2</sup>/°C (at a chilled water flow rate of 25 L/min and a bottoms flow rate of 0.1 L/min) with an LMTD at normal operating conditions of 74°C. This combination provides a duty of at least 400 W. The surplus duty is desirable for start-up and non-optimal operation where the bottoms rate might be significantly higher than the expected design rate of approximately 0.1 L/min.

## 11.5 FEED AND PRODUCT SYSTEMS

### 11.5.1 Hydrocarbon Feed Storage

The vapour pressure of the hydrocarbon that was obtained from Kwinana Refinery was estimated to be 200 kPag at 25°C. Therefore, in order to contain it as a liquid, it must be held under pressure or continuously chilled. The normal boiling point of -7°C makes chilling difficult so that pressurised storage was preferred. Compressed gas cylinders (e.g. butane, LPG, etc.) are typically rated to 3.3 MPa and are available in various volumes. These vessels were considered suitable for the present application and two 45 kg cylinders were leased to store the hydrocarbon. Unfortunately, the cylinders are equipped to discharge vapour only so that additional equipment is required to provide a liquid feed for the pilot plant. This is described in Section 11.5.2.

### 11.5.2 Feed Tanks

A dual feed tank system was installed. The first, smaller tank operates at above atmospheric pressure (up to 220 kPag) and is used to process raw feed through the column. The second, larger tank, operates at atmospheric pressure and is used when sufficient ETBE has been produced to increase the boiling point of the feed mixture to above the ambient temperature. Both feed tanks can be isolated with ball valves and connected to the feed pump suction.

The composition of the feed must be controlled to ensure the ethanol excess is within acceptable limits. This is achieved by measuring the weight of components as they are added to the feed tank using a set of accurate ( $\pm 100$  g) bathroom scales. Hydrocarbon is measured by difference while ethanol can be weighed directly. The ethanol must be introduced to the feed tank first to allow the hydrocarbon vapour to be bubbled through the mixture (the vapour inlet is located at the bottom of both feed drums). A cross-over line was added to the system to permit the hydrocarbon vapour to be passed through the bottoms cooler and partially condensed before being introduced to the feed tank. This increases the rate at which hydrocarbon can be added to the feed tank(s) since the flow rate is dependent on the pressure difference between the cylinder and the tank, and the pressures are direct functions of the temperature and composition in each vessel. Where the hydrocarbon concentration in the feed tank is high, the vapour pressure in the tank is similar to the pressure in the cylinder so that a temperature differential is required to provide an adequate flow rate.

### 11.5.3 Feed Pump

A helical rotor feed pump was selected to transport the feed mixture to the column. The helical rotor pump provides a continuous flow (rather than a surging flow from a diaphragm pump) and was significantly cheaper than a centrifugal pump for the combination of small flow and medium head required. A speed controller provides accurate flow control. The NPSHR of the pump is negligible but the feed tanks are elevated to ensure the suction is always flooded. An air bleed (used to prime the pump) and a drain (to empty the feed tanks) were also installed in the suction line. A non-return valve was installed in the discharge line so that the pump can be stopped and started while the column is operating under pressure.

The discharge line includes a pressure gauge to detect blockages between the pump discharge and the column. Since the pump operates via positive displacement, very high pressures are achievable. Therefore, a serious blockage has the potential to result in a pump failure if not detected promptly. Shortly after commissioning, rubbery organic solids were detected in the feed tank and at various downstream locations. These are tolerable with respect to the pump but might lead to blockages in the feed distributor or elsewhere. A strainer was installed to collect particles larger than  $270\text{ }\mu\text{m}$ .

### 11.5.4 Distillate Product

The distillate product has a similar composition to the raw hydrocarbon feed with isobutene removed by reaction. The distillate vapour pressure and boiling point are, therefore, similar to the feed and pressurised storage is again required. Two more 45 kg pressure cylinders



were obtained and were installed in parallel. Only one cylinder is used at a time. When full, an empty cylinder can be switched into line before shutting off the distillate flow to the full cylinder.

#### **11.5.5 Ether Product**

The boiling point of the ETBE product depends strongly on its purity from below ambient temperature where excess hydrocarbon is included in the bottoms to 70°C at an ETBE purity of 96%. Pressurised storage is not required provided the product can be cooled satisfactorily from the column operating temperature. A 205 L drum is used to collect the product. A cap on top of the drum prevents excessive loss of flammable vapour through evaporation. Sub-optimal operation will result in a much larger than normal concentration of ethanol in the ether product. However, the boiling point of ethanol is also safely above ambient temperatures. If necessary, the bottoms product can be recycled to either feed tank if atmospheric collection is not appropriate.

### **11.6 INSTRUMENTATION**

#### **11.6.1 Pressure Indicators and Transmitters**

There are four analog pressure gauges installed on the pilot plant. A panel mounted gauge indicates the column overhead pressure. A second panel mounted gauge indicates the pressure downstream of the bottoms control valve. Note that following a piping revamp, the difference between these two gauges is not indicative of the column pressure drop and cannot, therefore, be used to detect the onset of flooding. A third pressure gauge indicates the pump discharge pressure (as described in Section 11.5.3). The fourth gauge is mounted on the top of the pressurised feed tank and provides a continuous indication of the tank pressure.

A pressure transmitter measures the column overhead pressure (duplicating the reading from the first analog gauge). The transmitter signal (4-20 mA) can be used as a controller input to provide closed loop pressure control via the distillate control valve.

#### **11.6.2 Temperature Indicators and Transmitters**

Thermocouples were installed at five points over the length of the column and at the condenser outlet. The thermocouples are connected to a switching unit and to a panel mounted display. Only one temperature can be viewed at a time. The display also produces a 4-20 mA signal that can be used as a controller input, if required. The thermocouple

labels and positions are shown in Table 11.5. Each measurement is accurate to approximately  $\pm 0.1^\circ\text{C}$ .

Table 11.5 - Thermocouples

Label	Location
T1	Condenser outlet
T2	Column overhead
T3	Above reactive section
T4	Above stripping section
T5	Mid-stripping section
T6	Column bottom

### 11.6.3 Flow Indicators and Transmitters

There are flow meters in the reflux line, distillate line and bottoms lines. The meters all operate by displacement and magnets in dual rotors cause a reed switch to close once every rotation. This provides a pulsing signal that is interpreted by a display unit mounted on the main instrumentation panel. A selector switch determines which flow reading is displayed. The distillate and bottoms flow meters are identical. Each is accurate to  $\pm 1.0\%$  of the actual flow over the range 0.08-5.0 L/min and is pressure rated to 520 kPa. However, the construction of the meters has been modified to permit operation at higher pressures and they have been located downstream of the control valves to avoid exposure to the full column pressure. The reflux flow meter is accurate to  $\pm 0.5\%$  of the actual flow over the range 0.5-30 L/min and is rated to 8500 kPa. The volume per pulse from the reflux meter differs from the other two meters so that the displayed reading must be multiplied by a factor of 1.24 to indicate the actual flow rate. The display unit transmits a 4-20 mA signal that can be used as a controller input. Note that changing the selector switch will affect the signal to the controller so that this should only be done when the controller is in manual (open-loop).

### 11.6.4 Level Indicator and Transmitter

The level in the reboiler sump is shown via a sight glass at the base of the column. The upper tapping point is just above the windows in the reboiler baffle. The sight glass (custom made,  $\frac{3}{8}$  in. diameter borosilicate glass) can be isolated, if necessary, and is protected by a perspex shield. The same tapping points are connected to a differential pressure (dP) transmitter so that the level can be controlled automatically via the bottoms draw rate. The transmitter signal is dependent on the liquid density (estimated at  $700 \text{ kg/m}^3$  at normal

operating temperature) which varies with temperature so that some discrepancy with the sight glass indication is possible.

## 11.7 CONTROL SYSTEM

An automatic control system was installed on the pilot plant. The basic system consists of three regulatory loops that stabilise the process and permit manual or one-point composition control. A fourth loop can be closed to provide two-point composition control or alternative one-point configurations.

Unlike the industrial columns that were discussed in Chapters 8 and 10, the pilot plant has only four degrees of freedom since there is no reflux accumulator. The variables pairings are, therefore, somewhat different from a conventional column. Initially, the column pressure was controlled by manipulating the distillate rate, the reboiler level was controlled by manipulating the bottoms draw rate and the reflux rate was flow controlled. However, the equipment is sufficiently flexible to allow the variable pairings to be changed, as required, to investigate and test other combinations.

The configuration of the basic elements of control hardware is indicated in Figure 11.7. The three control loops (i.e. the loops which manipulate the process via the three control valves) which are depicted with solid lines are the basic loops described above. The fourth control uses the voltage regulator as a final control element instead of a control valve. This is feasible as it can receive and interpret a 4-20 mA signal from the controller. This control loop is depicted with dashed lines to indicate that it was initially operated in open-loop (i.e. the voltage is fixed independently of the controllers).

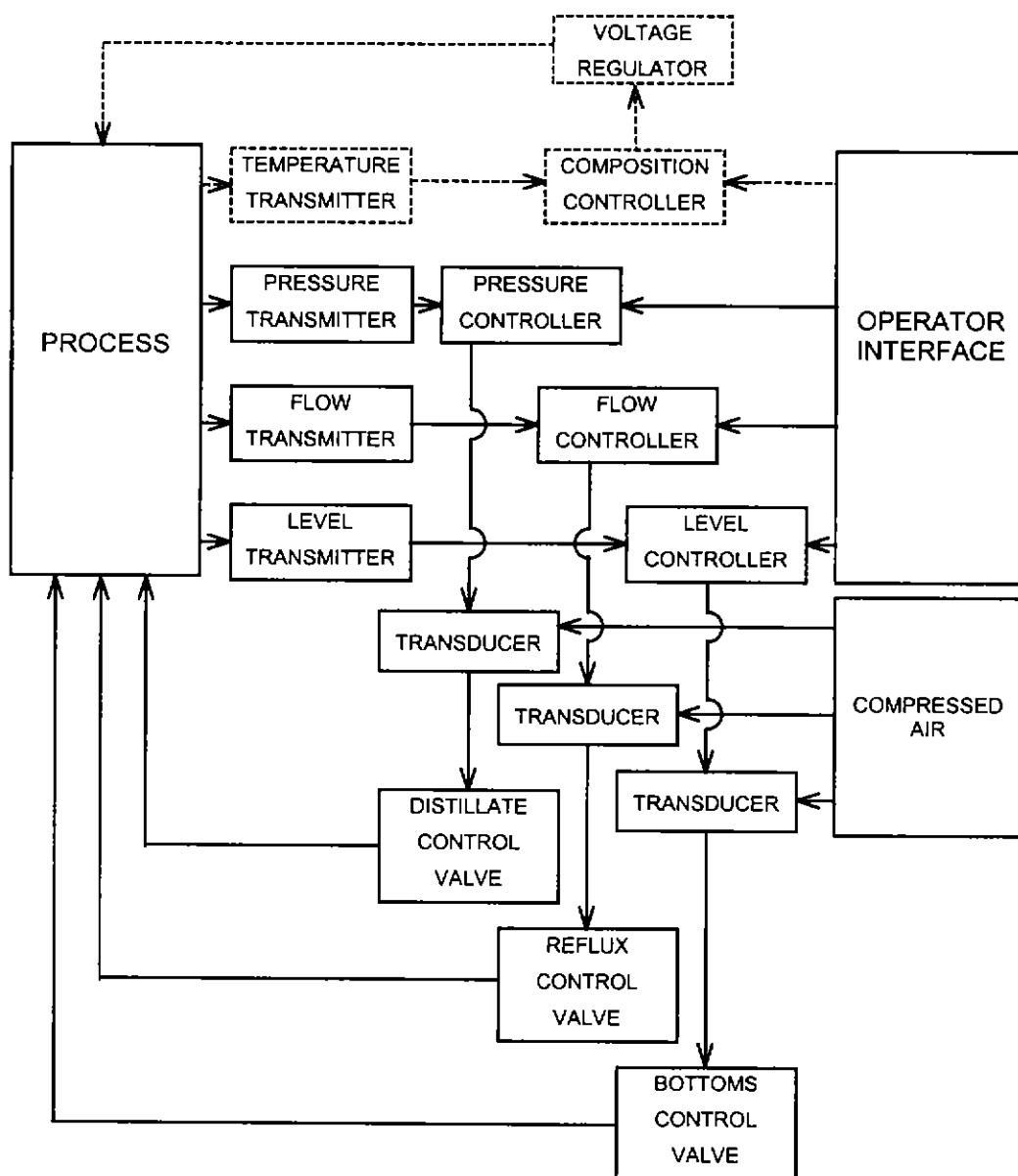


Figure 11.7 - Control System Block Diagram

## 11.8 INSTALLATION IN THE LABORATORY

The column is mounted on a customised frame for operation in the laboratory. The column is supported from the top by a pulley and at four points over its length by clamps fixed to the frame. The overhead condenser is hung from a roof beam by lightweight chain. The feed tanks sit on a raised platform while the feed and product cylinders, and the product tank sit on the ground. All cylinders are chained in place in accordance with regulatory requirements. The feed pump is bolted to the laboratory floor. The bottoms cooler is mounted on the wall behind the column.

The piping is mostly supported on the main frame or attached to the rear wall. Compression joints were used almost exclusively during installation to simplify assembly and disassembly. The various components of the instrument air system are also mounted on the rear wall. The main instrument panel is connected to the column frame and bolted to both the floor and rear wall. As far as possible, the instrument displays and electrics are separated from the piping and other equipment to avoid the possibility of leaks interfering with the electrical circuitry. Sample points were installed for both products so that samples can be taken for compositional analysis at various times during a test run. Figure 11.8 indicates the piping layout and the location of the instrumentation (i.e. the P&ID).

The control equipment was mounted in a separate control box that is located on a bench near the pilot plant. A personal computer (a Pentium 120) sits adjacent to the control box and serves as the operator interface using SCAN 3000 software.

## 11.9 COSTS

Itemised costs for all equipment used in the construction of the pilot plant are given in Table 11.6 excluding labour. The vendors and suppliers are indicated where standard Curtin University materials were not used. Some of the costs have been estimated where accurate data was not available or could not be found. The total cost, spent over a period of two years, was approximately \$27,000.

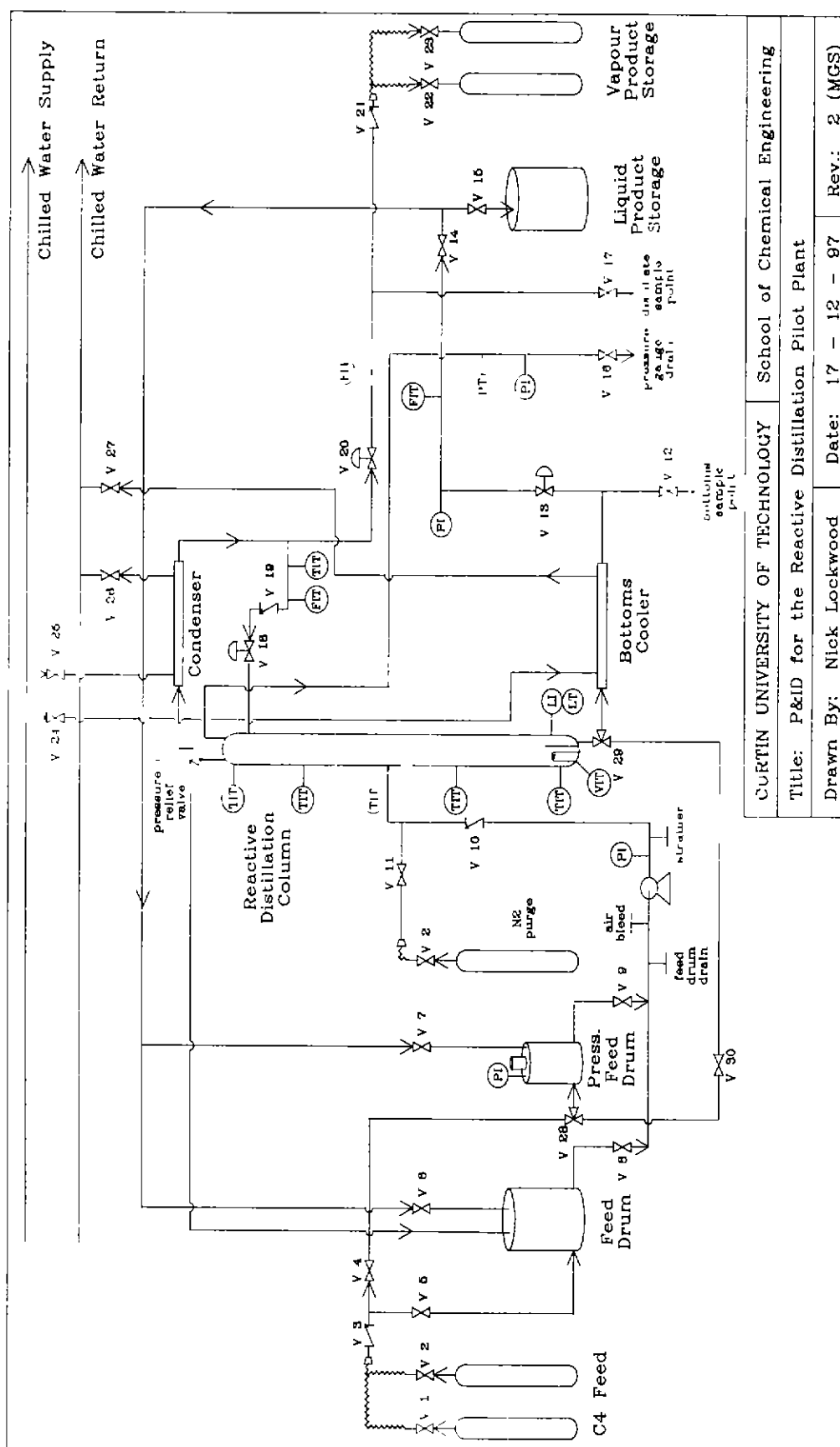


Figure 11.7 - Piping &amp; Instrumentation Diagram (P&amp;ID) for the Reactive Distillation Pilot Plant

Table 11.6 - Pilot Plant Capital Costs

Item	Vendor	Cost
<i>Non-Consumables</i>		
Column materials (shell, ends and flanges)		\$1897
Novel structured packing	Expamet	\$512
Electric elements	JG Thomas	\$395
Variable frequency drive	NHP Electrical Engineering	\$2200
Insulation	CSR Building Materials	\$205
Seals (o-rings)	Transeals	\$225
Feed and product tanks (non-pressure)		\$85
Pressurised feed tank	Bendigo Metals	\$688
Pressure cylinders and hoses	Kleenheat	\$660
Feed pump (including new stator)	Challenge Pumps (Mono)	\$3416
Stainless steel tube		\$550
Compression fittings, elbows, joints, etc.	Perth Valve & Fitting	~\$1200
Valves (including PRV and NRVs)	Braeco, Perth Valve & Fitting	\$1430
Sight glass	Glen Whiting	\$25
Pressure gauges	Braeco, Budenberg	\$689
Thermocouples and digital display	Technitemp	\$893
Flow meters and digital display	Hinco	\$1762
Pressure transmitter, differential pressure transmitter, controllers (3)	Honeywell	\$5000
Ammeter	NHP Electrical Engineering	~\$120
Rotameter	RS Components	\$102
Control valves (1 x ½ in., 2 x ¼ in.)	Western Process Controls	\$2796
Transducers (3)	AMS Technical services	\$909
Air regulator and filter		nil
Air hoses and fittings	Fluidair Services	\$119
Digital bathroom scales	Bunnings	\$56
Scaffolding and frame		~\$400
Sub-Total		\$26,334
<i>Consumables</i>		
Hydrocarbon feed	BP, Kwinana Refinery	free
Ethanol		\$322
Catalyst	Rohm & Haas	\$300
Sub-Total		\$622
Total Installed Cost		\$26,956

## **CHAPTER TWELVE**

### **EXPERIMENTAL TESTS**

- 12.1 Equipment Tests**
  - 12.1.1 Novel Structured Packings
  - 12.1.2 Reactive Packings
  - 12.1.3 Feed Pump
  - 12.1.4 Bottoms Cooler
  - 12.1.5 Reboiler
  - 12.1.6 Condenser
- 12.2 Pilot Plant Simulations**
- 12.3 Operating Procedures**
  - 12.3.1 General Procedures
  - 12.3.2 Start-Up Procedure
  - 12.3.3 Shut-Down Procedure
  - 12.3.4 Emergency Response
- 12.4 Total Reflux Tests**

### **12.1 EQUIPMENT TESTS**

#### **12.1.1 Novel Structured Packings**

The novel structured packings that were used in the non-reactive sections of the column (i.e. the rolled mesh bales described in Chapter 11, Section 11.3.2) were tested prior to installation in the column in order to determine the pertinent packing characteristics: capacity, holdup, radial dispersion and pressure drop. The tests were performed in an apparatus used for undergraduate mass transfer laboratory experiments using air and water as the test fluids. The test rig diameter (140 mm) was similar to the pilot plant column (155 mm) and was constructed of perspex so that the fluid flow patterns could be observed.

A water flow rate of 3.5 L/min was used for all the tests while the air flow was varied from 150 L/min to 800 L/min. These rates compare with the pilot plant design conditions of 3.3 L/min of liquid and 60 L/min of vapour. The tests were repeated with 6 mm glass Raschig rings to provide a secondary assessment of the packing characteristics. These data were considered important since flooding predictions obtained with Pro/II indicated that 6 mm raschring rings would provide adequate hydraulic capacity for the required service. The pressure drop data from both sets of tests are shown in Table 12.1 and indicate that the



novel packings have a higher capacity than the raschring rings, suggesting satisfactory hydraulic performance in the pilot plant.

**Table 12.1 - Air-Water Pressure Drops for Novel Structured Packings and 6 mm Glass Raschring Rings in the 140 mm Diameter Test Apparatus**

Air Flow (L/min)	Novel Structured Packings		6 mm Raschring Rings	
	$\Delta P$ (mm H <sub>2</sub> O)	$\Delta P/m$	$\Delta P$ (mm H <sub>2</sub> O)	$\Delta P/m$
150	2.5	10	3	12
200	3	13	4.5	19
300	5	21	10	42
400	7	29	18	75
500	11	46	28	117
600	15	63	45	188
800	26	109	flooding	flooding

The higher density of the process vapour compared with the test fluid (air) will increase the pressure drop from the measured values but, at a vapour flow of 60 L/min, flooding is not expected in the pilot plant. The holdup and radial dispersion of the novel packings were recorded visually and were found to be similar to the raschring rings and, therefore, were considered to be acceptable.

### 12.1.2 Reactive Packings

The design of the reactive packings was developed by assessing the packing characteristics of several configurations in the same rig that was used to test the non-reactive packings. Flooding was experienced in the packed column apparatus for all materials and catalyst loadings using the sachet design (Chapter 11, Figure 11.2a) with a liquid flow of 2.5 L/min and a vapour flow of 120 L/min. The catalyst bale design (Figure 11.2b) provided sufficient capacity to prevent flooding at moderate to high air and water flows. The measured data are indicated in Table 12.2 with calculated dimensionless parameters for the Eckert generalised pressure drop correlation (GPDC) (Kister, 1992). The generalised parameters permit the packing factor to be estimated for both types of reactive packings (Table 12.2).

Table 12.2 - Hydraulic Capacity of Catalyst Bales (Air-Water Tests)

Configuration	Air (L/min)	Water (L/min)	$\Delta P$ (mm H <sub>2</sub> O)	Flow Parameter	Capacity Parameter	Packing Factor
Basic catalyst bale	200	2.5	12	0.36	0.035	1860
	300	3.5	47	0.34	0.058	1370
Catalyst bale with mesh interleave	200	2.5	7	0.36	0.030	1590
	300	3.5	22	0.34	0.045	1060

The capacity parameter and flooding point can be estimated for the expected operating conditions using the estimated packing factors determined with the air-water tests. This data is shown in Table 12.3 and indicates that both the basic catalyst bale or the catalyst bale with mesh interleave have sufficient hydraulic capacity. Although the capacity parameter is equal to the flooding point for the basic catalyst bale (i.e. 100% flooding factor), the high pressure drop that was observed with the air-water tests without the onset of flooding generate confidence that flooding will not be experienced in the pilot plant column. Although the use of the catalyst bale with mesh interleave would provide greater certainty that flooding will be avoided, the basic catalyst bale design was preferred since it was considered to provide a larger liquid contact surface which should promote the reaction.

Table 12.3 - Expected Operating Conditions for the Catalyst Bales

Configuration	Flow Parameter	Capacity Parameter	Flood Point	Acceptable?
Basic catalyst bale	0.13	0.12	0.12	✓
Catalyst bale with mesh interleave	0.13	0.10	0.12	✓

### 12.1.3 Feed Pump

The feed pump was calibrated against the vendor's pump curve by collecting volumes of ethanol from the pump discharge through the nitrogen purge valve. The results are shown in Figure 12.1 and indicate the pump performance is only slightly below expectation.

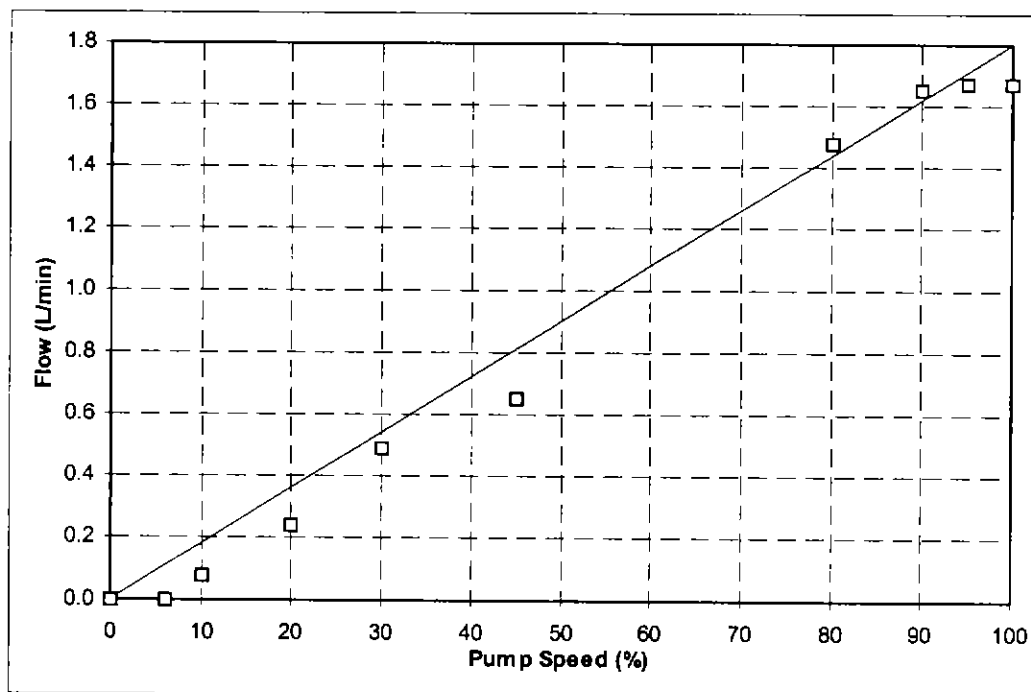


Figure 12.1 - Feed Pump Performance and Design Curve

This test was repeated regularly to ensure that the pump speed could be used to accurately infer the feed rate. Unfortunately, a significant deterioration in performance was detected on several occasions indicating damage to the stator. Such damage could have initially been caused by operating the pump before the stator was sufficiently wetted but subsequent failures are suspected to be linked with material incompatibility. Neither Viton nor Buna-N (nitrile) stators provided sustained satisfactory performance. It was speculated that the failures could have been caused by acetic acid (created through oxidation of ethanol), trace amounts of benzene that were contained in the ethanol or trace amounts of hydrofluoric acid contained in the hydrocarbon from the Kwinana Refinery alkylation unit.

### 12.1.4 Bottoms Cooler

Several sets of temperature measurements were taken during the operation of the pilot plant to assess the performance of the bottoms cooler. The inlet and outlet chilled water temperatures are not measured on-line but a surface temperature probe was used to provide this data for various process conditions. Similarly, the chilled water flow to the bottoms cooler would not normally be manipulated during the operation of the pilot plant but two

flow rates were examined for the purpose of evaluating the heat transfer rates. The data is shown in Table 12.4 and compared with the predicted heat transfer coefficients (HTCs) in Figure 12.2. The excellent agreement between the measured and predicted values confirms the appropriateness of the design method and suggests that the bottoms cooler can provide adequate cooling at the expected operating conditions.

Table 12.4 - Heat Transfer Data for the Bottoms Cooler

Inner Pipe			Outer Pipe					
Flow	Inlet Temp.	Outlet Temp.	Flow	Inlet Temp.	Outlet Temp.	LMTD	Duty	HTC
(L/min)	(°C)	(°C)	(L/min)	(°C)	(°C)	(°C)	(kW)	(W/°C/m <sup>2</sup> )
0.27	106.9	35.3	20	9.7	10.0	53	0.60	376
0.30	102.0	35.1	20	9.7	10.0	52	0.62	404
0.23	98.6	35.6	10	9.6	10.2	51	0.45	297
0.22	92.3	34.1	10	9.5	10.1	48	0.40	281

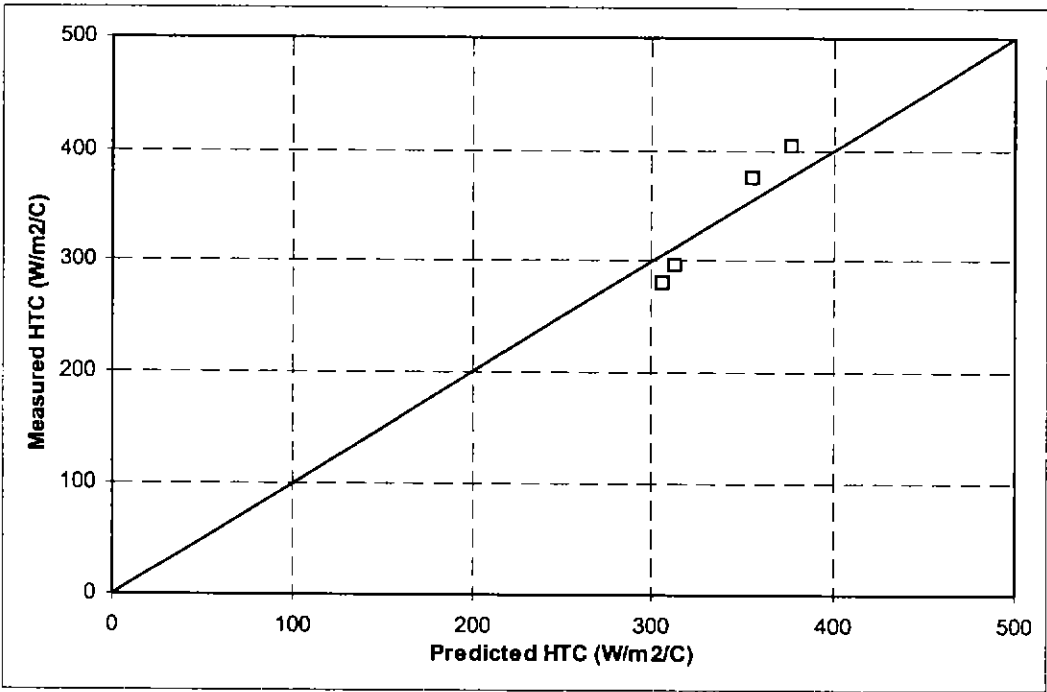


Figure 12.2 - Measured and Predicted Heat Transfer Coefficients for the Bottoms Cooler

### 12.1.5 Reboiler

The reboiler heating elements were designed (by the vendor) to supply a maximum of 7.5 kW at 240 V of three phase power. This was tested by recording the rate at which the reboiler sump temperature increased from ambient with a given reboiler voltage. Two reboiler tests were conducted: 120 V and 180 V. In both cases, the initial reboiler sump volume was 9.5 L. The raw data and instantaneous heating rates are shown in Table 12.5 and the heating rates are plotted in Figure 12.3.

Table 12.5 - Transient Heating Data for the Reboiler

120 V			180V		
Time (mins)	Temperature (°C)	Instantaneous Duty (kW)	Time (mins)	Temperature (°C)	Instantaneous Duty (kW)
0	22.2	-	0	28.2	-
1	22.3	0.03	1	28.7	0.15
2.5	23.5	0.24	1.5	29.9	0.59
3	31.4	4.69	2	35.7	3.56
3.5	37.9	3.86	2.5	49.8	8.38
4	44.6	3.98	2.75	55.5	6.77
4.5	52.1	4.46	3	60.7	6.18
5	58.7	3.92	3.25	65.0	5.11
5.75	67.0	3.29	3.5	68.1	3.68
6	68.6	1.90	3.75	71.0	3.45
6.5	72.0	2.02	4	73.0	2.38
7	74.7	1.60			

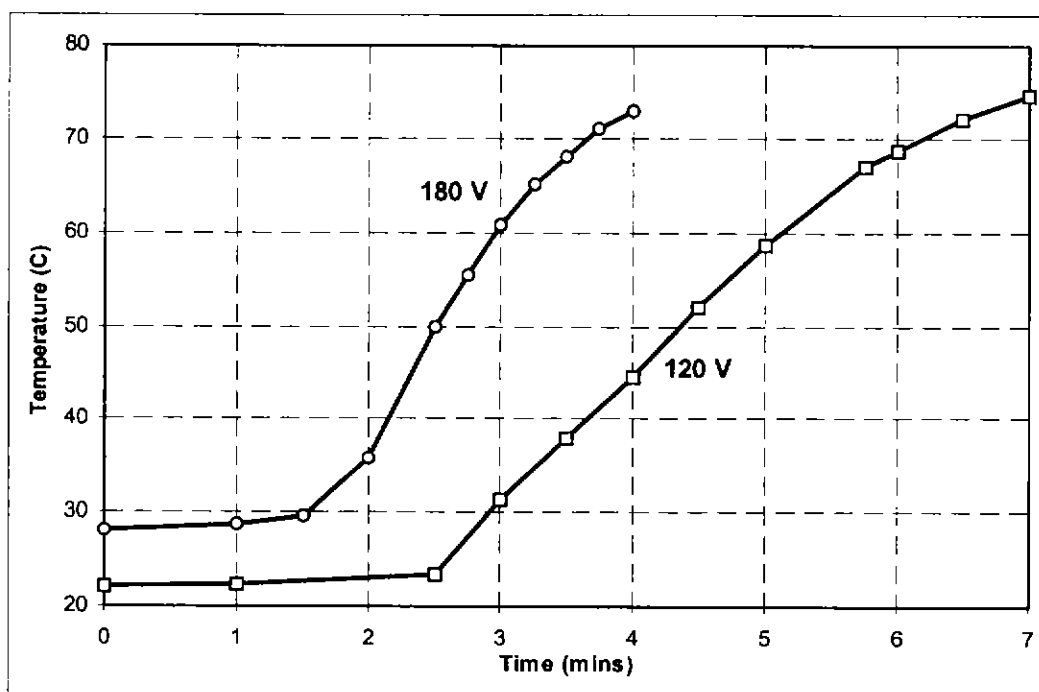


Figure 12.3 - Heating Rate at 120 V and 180 V

The reboiler elements take some time to reach operating temperature (approximately 220°C) and the heating rate is unrepresentative of the normal process during this period. Immediately after this initial period, there will still be negligible vaporisation of liquid and the supplied duty will essentially produce sensible heat transfer only. Thereafter, the (unmeasured) latent heat effects will predominate and only part of the energy input can be measured via sensible heat changes so that the heating rate is, again, unrepresentative of the normal process. The actual reboiler duties can be calculated from the maximum gradient of each curve in Figure 12.3 according to the first principles formula given by equation (12.1).

$$Q = m \times c_p \times \frac{dT}{dt} \quad (12.1)$$

With these considerations, the reboiler elements were estimated to produce 4.2 kW of heating power at 120 V and 7.8 kW at 180 V. The three-phase power output of a mainly resistive element should be calculable from the voltage (V), resistance (R) and the phase angle ( $\phi$ ) via equation (12.2). This relationship suggests that the power will be proportional to the square of the voltage for constant resistance and phase angle. However, this is inconsistent with the reboiler data suggesting a dependence between the operating temperature and the resistance or the phase angle.

$$Power = V^2 \times R \times \sqrt{\phi} \quad (12.2)$$

Insufficient data could be collected at 240 V since boiling began soon after the elements reached operating temperature but the duty was estimated to be 12.1 kW by extrapolation according to the empirical relationship indicated by equation (12.3). This estimated maximum duty is significantly higher than the design duty and suggests that a voltage of 150-180 V will be adequate for most conditions.

$$Power = 0.0028 \times V^{1.53} \quad (12.3)$$

### 12.1.6 Condenser

It was not possible to adequately assess the performance of the condenser during normal operation due to difficulties in stabilising and accurately measuring the reflux rate. Therefore, extensive tests were completed with hot water flowing through the inner pipe with various inlet temperatures and flow rates. The results of these tests are shown in Table 12.6. The chilled water flow could not be measured and was calculated via an energy balance. The heat transfer coefficients calculated from this data are not directly applicable to the expected operating conditions (e.g. no phase change in the inner pipe and different physical properties) but were used to estimate the fouling resistance of the condenser during normal operation. This data was then applied to the original design basis to calculate the heat transfer coefficient at the expected operating conditions.

The measured and predicted heat transfer coefficients for the test data for various values of the fouling resistance are displayed in Figure 12.4. This data indicates that no value of the fouling resistance provides a satisfactory agreement between the measured and predicted heat transfer coefficients: the HTC is generally overestimated where low and underestimated where high. The discrepancy is probably due to changes in the flow regime and Figure 12.5 shows that the predictions are mostly accurate for turbulent flows but optimistic for laminar and transitional flows (say,  $Re < 6000$ ). Since the expected operating conditions for the condenser lie in the turbulent flow regime, a fouling resistance of  $0.0003 \text{ m}^2 \cdot ^\circ\text{C}/\text{W}$  was assumed to predict the actual condensing performance. This corresponds to a heat transfer coefficient of  $1274 \text{ W}/\text{m}^2 \cdot ^\circ\text{C}$  and a heat transfer rate of greater than 20 kW.

The calculated heat transfer duty that is available from the condenser greatly exceeds the design cooling duty (7.3 kW) and, therefore, suggests satisfactory condenser performance. However, the effects of small amounts of non-condensibles (e.g. nitrogen that remains in the

column after purging) could not be accounted for and could possibly reduce the heat transfer rate considerably. It will be important to minimise non-condensibles by venting some of the distillate as vapour during start-up. Furthermore, the fouling resistance contributes 30-50% of the total heat transfer resistance and fouling with a higher resistance than that which is anticipated will cause a noticeable deterioration in condenser performance.

**Table 12.6 - Heat Transfer Data for the Condenser**

Inner Pipe			Outer Pipe					
Flow	Inlet Temp.	Outlet Temp.	Flow	Inlet Temp.	Outlet Temp.	LMTD	Duty	HTC
(L/min)	(°C)	(°C)	(L/min)	(°C)	(°C)	(°C)	(kW)	(W/°C/m <sup>2</sup> )
0.62	47.8	11.0	57	7.2	7.6	15.4	1.52	412
0.83	49.6	12.5	44	7.0	7.7	17.9	2.35	548
0.88	42.9	13.9	36	8.5	9.2	15.5	1.77	478
1.12	43.7	11.7	51	7.2	7.9	15.1	2.52	698
1.45	38.2	11.0	56	7.3	8.0	12.6	2.65	877
1.46	40.0	13.8	35	8.6	9.8	14.1	2.65	785
1.78	44.6	13.7	42	8.7	9.9	15.4	3.81	1032
2.04	38.1	13.1	39	8.8	10.1	12.6	3.54	1167
2.29	63.5	14.4	56	7.4	9.4	23.0	7.57	1373
2.40	37.6	14.0	40	8.9	10.3	13.2	3.93	1239
2.60	49.5	15.3	30	8.3	11.3	18.4	6.33	1439
2.85	50.6	14.0	55	7.0	8.9	19.4	7.10	1525
3.47	38.0	13.8	31	8.0	10.7	13.9	5.83	1756
3.53	63.5	17.5	52	7.0	10.1	26.4	11.31	1792
3.72	36.3	13.2	53	7.1	8.7	14.2	5.91	1733
4.22	60.5	20.5	38	8.7	13.1	25.6	10.61	1731
4.46	63.5	20.4	53	7.6	11.2	28.1	13.26	1974
4.59	38.8	15.5	33	8.0	11.2	15.4	7.17	1941



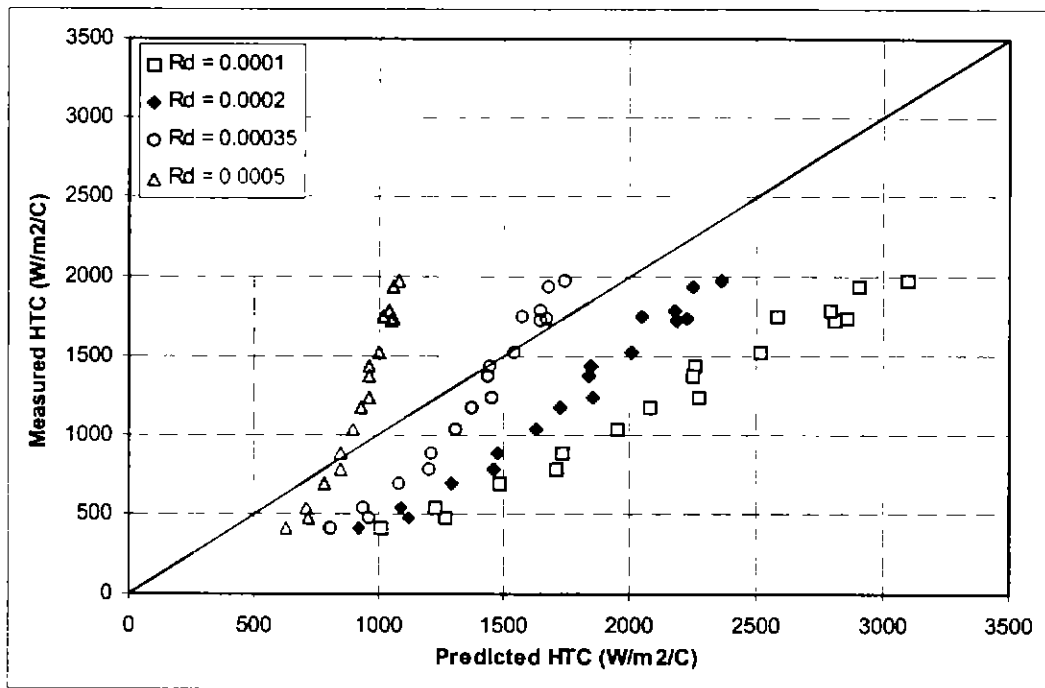


Figure 12.4 - Predicted and Measured HTC for the Condenser (Test Conditions)

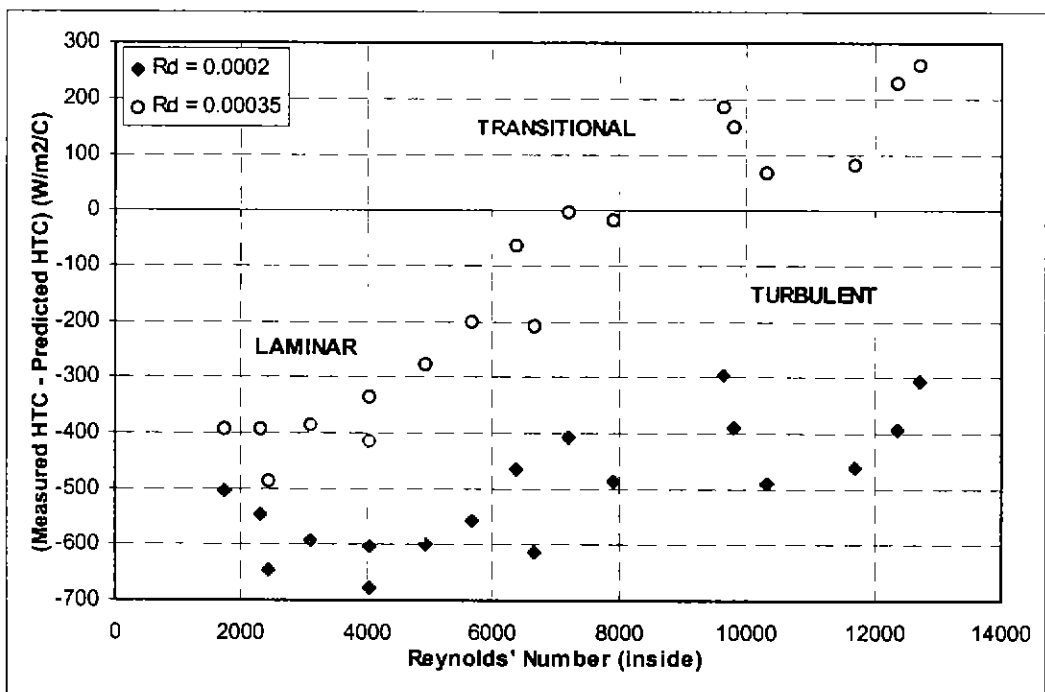


Figure 12.5 - Effect of Flow Regime on the Heat Transfer Correlation

## 12.2 PILOT PLANT SIMULATIONS

Simulations of the pilot plant configuration had previously been performed using both Pro/II and SpeedUp (Chapter 11). However, these models were used for design and did not reflect the actual process exactly. Specifically, the pilot plant is operated by specifying five conditions: three valve positions, the pump speed and the reboiler voltage. This contrasts with the design models where the feed rate, the operating pressure, the reboiler duty, the reflux rate and the bottoms rate (or similar combinations) were specified. The flexibility of the SpeedUp simulation environment was utilised to develop another model of the pilot plant that matched the actual pilot plant inputs. This model was used to provide additional information regarding the operation of the pilot plant and can be used to detect equipment failures (e.g. fouling, blockages, poor heat transfer, etc.) via disparities between the process and the model.

The pilot plant was commissioned with a feed mixture containing predominantly ethanol to simplify handling and storage. The operating conditions are predicted by the simulation and are shown in Table 12.7. More importantly, the simulations can be used to predict the transient response of the process to changes in the key operating variables. Figure 12.6 indicates the process response to closing the reflux control valve by 0.5%, Figure 12.7 shows the response to an increase in the reboiler voltage and Figure 12.8 indicates the response to an increase in the feed pump speed.

Table 12.7 - Predicted Operating Conditions for Commissioning Feed

=====					
INPUT CONDITIONS					
-----					
	ETHANOL	ISOBUTENE	ETBE	N-BUTENE	
FEED COMP (wt percent)	71.1	3.5	0	25.4	
FEED COMP (mole percent)	75.0	3.0	0	22.0	
FEED TEMPERATURE	15.0 C				
FEED RATE	0.51 L/min		30.0 percent		
COLUMN PRESSURE	800.0 kPa-g				
REFLUX RATE	1.25 L/min				
REBOILER DUTY	7.24 kW		170.0 V		
REFLUX CONTROL VALVE	95.0 percent closed				
DISTILLATE CONTROL VALVE	99.5 percent closed				
CONDENSER FLOODING	31.5 percent				
=====					
OUTPUT CONDITIONS					
-----					
TEMPERATURE AND COMPOSITION PROFILES (mole percent)					
-----					
	TEMP	ETHANOL	ISOBUTENE	ETBE	N-BUTENE
CONDENSER	75.1	23.6	8.6	0.5	67.3
TRAY 2 (RECT)	101.9	84.9	1.5	0.8	12.8
TRAY 3 (RXN)	133.8	96.9	0.3	0.4	2.4
TRAY 4 (RXN)	138.2	98.2	0.2	0.2	1.4
TRAY 5 (RXN)	138.7	98.3	0.1	0.2	1.4
TRAY 6 (STRP)	138.7	98.4	0.2	0.1	1.3
TRAY 7 (STRP)	144.8	99.8	0.0	0.0	0.1
TRAY 8 (STRP)	145.4	100.0	0.0	0.0	0.0
TRAY 9 (STRP)	145.5	100.0	0.0	0.0	0.0
REBOILER	145.5	100.0	0.0	0.0	0.0
-----					
PRODUCTS		(wt percent)			
	RATE (L/min)	ETHANOL	ISOBUTENE	ETBE	N-BUTENE
DISTILLATE	0.262	20.14	8.97	0.99	69.89
BOTTOMS	0.389	99.99	0.0	0.01	0.0
-----					
ISOBUTENE CONVERSION		0.12 mole percent			
=====					

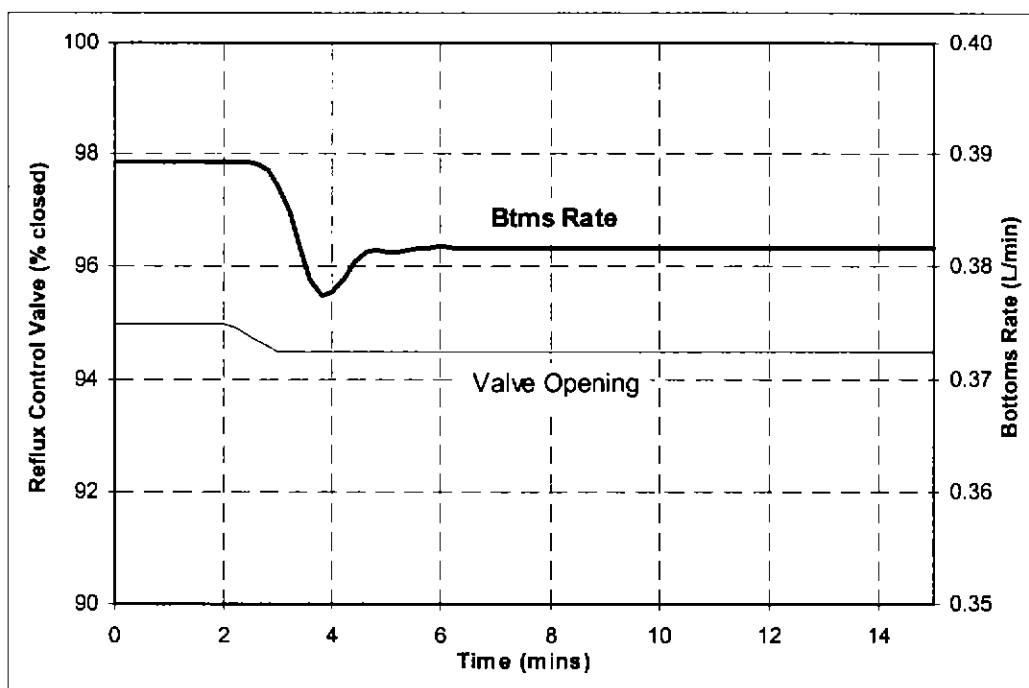


Figure 12.6 - Transient Response of the Pilot Plant to Closing the Reflux Control Valve

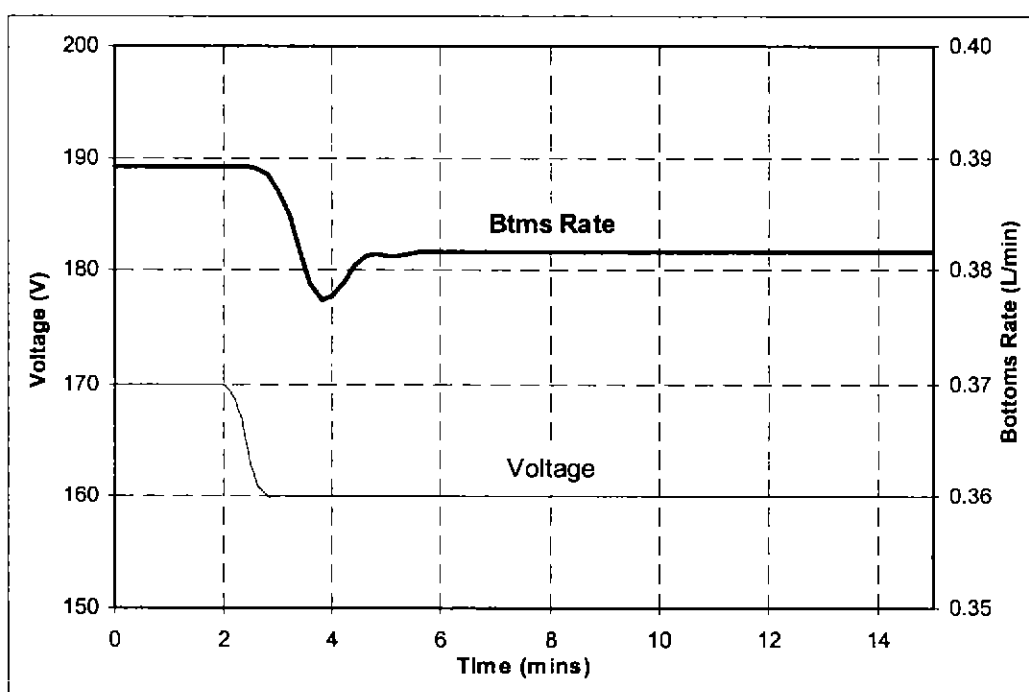
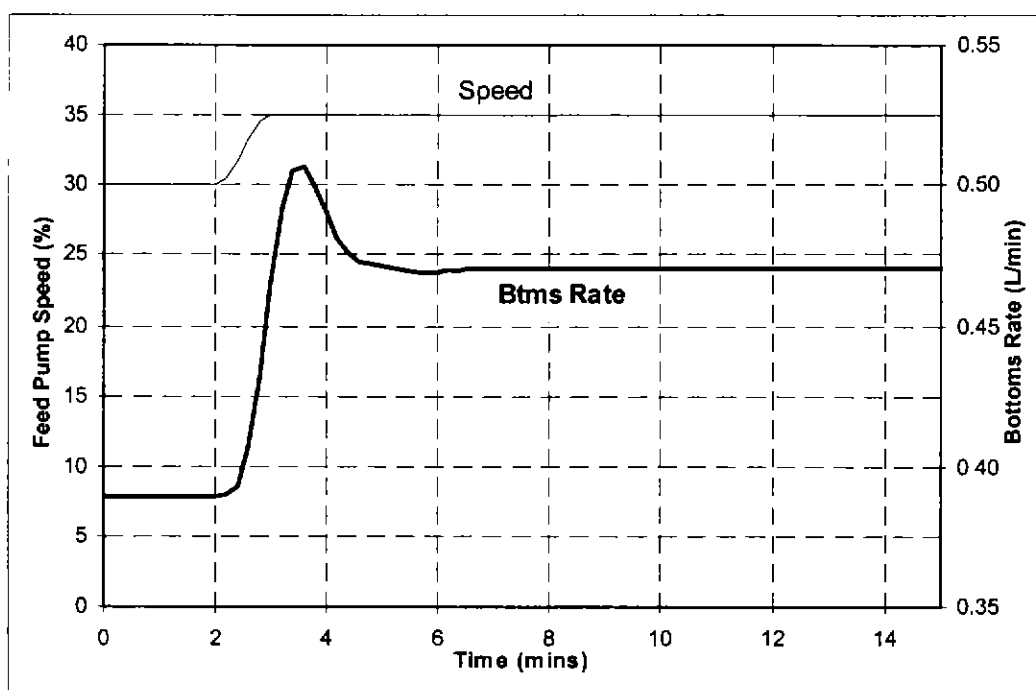


Figure 12.7 - Transient Response of the Pilot Plant to Decreasing the Reboiler Voltage



**Figure 12.8 - Transient Response of the Pilot Plant to Increasing the Feed Pump Speed**

Figures 12.6-12.8 indicate a dominant time constant of approximately 5 minutes. This is convenient since the effects of changes in the feed conditions and in the manipulated variables will be fully evident within a short time thereby allowing several tests to be conducted each time the pilot plant is operated. Figures 12.6-12.8 also indicate significant overshoot in the responses to changes in the reflux rate, reboiler duty and the feed rate. It will be important to consider this effect and allow the column to stabilise sufficiently before collecting data from the pilot plant.

## 12.3 OPERATING PROCEDURES

### 12.3.1 General Procedures

All activities associated with the pilot plant, including equipment tests, modifications, trial runs and production runs, should be recorded in the Reactive Distillation Pilot Plant Log Book which should be kept in the laboratory at all times. Safety inspections should be undertaken regularly (e.g. once per month) to ensure that the condition of the laboratory is maintained satisfactorily and that any deterioration in equipment is detected promptly. Examples of suitable safety checklists are included in Gibbons (1996) and Lockwood (1997).

### 12.3.2 Start-Up Procedure

An operating procedure for the pilot plant has been developed during commissioning and trial runs of the equipment. The procedure, outlined in Table 12.8, will continue to change as additional information is learned about the system and the specific quirks of the equipment are revealed. The crucial aspect of the operating procedure is safety and the necessity for common sense to be used at all times during the operation of the equipment is emphasised. The process fluids are potentially hazardous and care should be taken to avoid exposing the equipment to any ignition source before, during or after being operated.

**Table 12.8 - Start-Up Procedure for the Reactive Distillation Pilot Plant**

Step	Action Required
1	Check that all safety equipment is available and operational <u>before</u> beginning to operate any equipment in the laboratory (see Table 12.9). Check that the compressed air pressure is at least 300 kPa via the regulator gauge. Ensure that someone knows of your intention to operate the pilot plant or will be present while it is being operated.
2	Start the extraction fan and air conditioning to ensure the laboratory air is turned over at an acceptable rate.
3	Fill the feed tank with the desired mixture of ethanol and hydrocarbon. A known volume of ethanol should be introduced via the screw cap. The drum should be sealed tightly before introducing hydrocarbon from the cylinders via the bottoms cooler. Stop the flow periodically to weigh the cylinder in order to record the weight of hydrocarbon introduced to the feed mixture.
4	Check the orientation of all ball valves to ensure that the bottoms product will be recycled to the feed tank and that no distillate will be collected. Align the three way valves to prevent the flow of hydrocarbon to or from the feed cylinders. All samples points should be shut. The level column isolation valves should be open. All control valves should be fully closed (note that the 'off' position for the control valves is fully open).
5	Pressurise the column with nitrogen to 200 kPa and then depressurise to less than 10 kPa to reduce the oxygen partial pressure in order to prevent a flammable mixture forming inside the column. Repeat this step two further times if the column has recently been fully opened to the atmosphere.

6	Ensure that there is at least 20 L of feed available in the feed tank. Prime the pump, bleed any air from the pump vent and seal the vent when full of liquid. Check liquid flows from the pump drain. Check and clear (if necessary) the strainer on the pump discharge line.
7	Start chilled water flow to the bottoms cooler and condenser. Check the rotameter float is at or near the top of its range.
8	Turn on three phase power at the mains and switch on all instrumentation and equipment at the junction box.
9	Start the feed pump. Slowly open the bottoms control valve after the reboiler sump level reaches the middle of the level column. This ensures that the reboiler elements are fully covered. Adjust the bottoms control valve to maintain constant sump level near the top of the sight glass.
10	Turn the reboiler on and fix the voltage at approximately 180 V to bring the column towards operating pressure. Monitor the column temperature profile to determine when vapour has reached the condenser: the column temperature will increase as the vapour reaches that point; and the reflux temperature will decrease when condensation begins. Vent the distillate as vapour (to the product cylinders) for 5-10 minutes to purge the system of non-condensable gases.
11	Allow the liquid distillate volume to build up. <u>Slowly</u> open the reflux control valve to introduce reflux to the column. This will initially destabilise the column temperature profile and pressure - allow the column to return to steady state.
12	<u>Slowly</u> open the distillate control valve to control the column pressure at the desired value. Opening this valve too quickly will drain the distillate and stop the reflux flow.
13	Vary the reboiler voltage to control the feed split. Monitor via the column temperature profile. Refer to charts in the laboratory to estimate the bottoms composition from the temperature at a given pressure.
14	Adjust the reflux rate and compensate the column by changing the reboiler voltage and distillate control valve as required.

Table 12.9 - Safety Equipment

Item	Description	Requirements
1	Fire extinguisher	<ul style="list-style-type: none"> <li>• valid expiration date</li> <li>• suitable for hydrocarbon fires (e.g. dry CO<sub>2</sub>)</li> <li>• easily accessible</li> </ul>
2	Exhaust fan	<ul style="list-style-type: none"> <li>• operational</li> </ul>
3	Air conditioning	<ul style="list-style-type: none"> <li>• operational</li> </ul>
4	Drain	<ul style="list-style-type: none"> <li>• clear</li> </ul>
5	Instrumentation safety covers	<ul style="list-style-type: none"> <li>• mesh screens are in place</li> <li>• no exposed wires</li> </ul>
6	Power isolation switch	<ul style="list-style-type: none"> <li>• location known</li> <li>• easily accessible</li> </ul>
7	Feed tank vent line	<ul style="list-style-type: none"> <li>• clear</li> <li>• discharges outside laboratory</li> </ul>
8	Safety shower and eye bath	<ul style="list-style-type: none"> <li>• operational</li> <li>• water is cool</li> </ul>
9	First aid kit	<ul style="list-style-type: none"> <li>• available in adjoining laboratory</li> </ul>

### 12.3.3 Shut-Down Procedure

The pilot plant should be safely and efficiently shut-down at the end of every trial run. Under no circumstances should the feed pump or reboiler be left operational overnight or while the pilot plant is unattended. A shut-down procedure is outlined in Table 12.10 and, again, common sense and safety should be the primary focus at all times.

If necessary, a faster shut-down can be achieved by withdrawing distillate and collecting it in the product cylinders as either liquid or vapour. This action will reduce the column pressure and initiate rapid cooling as liquid vaporises throughout the column. However, this shut-down route potentially wastes hydrocarbon since it is difficult to recycle the distillate from the product cylinders.



Table 12.10 - Normal Shut-Down Procedure for the Reactive Distillation Pilot Plant

Step	Action Required
1	Turn the reboiler off. Continue to circulate chilled water through the condenser and the bottoms cooler. Continue to manipulate the bottoms control valve to keep the reboiler sump level stable.
2	Shut the distillate control valve as the column pressure begins to decrease. The reflux control valve can remain open.
3	Continue to recycle the bottoms product to the feed tank via the bottoms cooler. This will remove heat from the process and expedite the cooling of the equipment.
4	Stop the feed pump and close the bottoms control valve when the reboiler temperature falls below 60°C.
5	Stop the chilled water flow to the condenser and bottoms cooler and allow the column to cool further due to heat losses only.
6	Turn off power to the reboiler and feed pump but maintain power to the thermocouple display to provide a continuous indication of the temperature of the column.
7	Check the orientation of all ball valves to ensure that all sample points are closed and that the column is isolated.
8	Stop the extraction fan and air conditioning once the laboratory atmosphere is normal. Continue to circulate air through the laboratory (via the extraction fan and air conditioning) if a strong hydrocarbon or ethanol odour is detected.

#### 12.3.4 Emergency Response

In the event of an emergency, timely and appropriate action will be required to make the pilot plant safe as quickly as possible. The nature of the emergency will determine the correct course of action but the steps suggested in Table 12.11 are recommended in the absence of other directions.

**Table 12.11 - Emergency Shut-Down Procedure for the Reactive Distillation Pilot Plant**

Step	Action Required
1	Assess danger to plant and personnel. Advise any occupants of the adjoining offices to evacuate and raise the alarm if necessary.
2	Turn off the reboiler at the voltage regulator, if possible, or cut power to the pilot plant at the three-phase plug in the north-eastern corner of the lab or by pressing the emergency power isolation switch on the western wall of the laboratory.
3	Isolate the hydrocarbon feed cylinders. If the pressure is low, isolate the product cylinders too, otherwise relieve the pressure buildup to the product cylinders.
4	Stop the feed pump. Continue to circulate chilled water through the bottoms cooler and condenser and leave instrumentation operational to provide feedback on the condition of the column. Ensure that the feed tank is vented outside the laboratory.
5	Isolate the level column if the sight glass breaks.
6	Initiate standard shut-down procedures as soon as it is safe to do so.

## 12.4 TOTAL REFLUX TESTS

A series of tests was completed to determine the maximum reflux rate for various values of the reboiler voltage. The reboiler sump was filled with approximately 10.0 L of liquid (mostly ethanol) before the reboiler elements were turned on. The feed pump was stopped and both the bottoms control valve and the distillate control valve were fully closed. The chilled water flow to the condenser was maximised (i.e. approximately 50 L/min) and the reflux control valve was opened fully.

The column pressure was permitted to increase until the rate of condensation in the condenser exactly balanced the rate of vaporisation from the reboiler (i.e. the process reached steady state). At this time, the reflux rate was recorded via the flow meter and the condenser duty estimated from the chilled water inlet and outlet temperatures. This data provides a secondary measurement of the reflux rate to verify the flow meter reading which was suspect due to an intermittent instrumentation error. The reflux rate was also estimated via simulation (Pro/II) from the estimated reboiler duty which was calculated from the voltage by equation (12.3). Three different reboiler voltages, 100 V, 150 V and 180 V, were tested in this way with the results shown in Table 12.12.

Table 12.12 - Results of Total Reflux Tests

Reboiler		Condenser			Reflux Rate		
Voltage (V)	Est. Duty (kW)	Temps (°C)	Est. Duty (kW)	Pressure (kPa)	Meter (L/min)	Calc. (L/min)	Sim. (L/min)
100	3.2	9.0-10.5	5.2	390	n/a	0.51	0.30
150	6.0	9.9-12.4	8.7	460	0.56	0.86	0.58
180	7.9	7.9-9.5	5.6	840	0.61	0.61	0.84

The three different measurements of the reflux rate correspond reasonably but there are significant uncertainties associated with each reading: the meter reading should be accurate to within 1% but the display periodically resets to zero when there is a known flow of liquid so that the reading is biased towards zero (a filter was used to stabilise the reading); the calculated reflux rate is sensitive to slight changes in the chilled water temperatures and the uncertainty in the chilled water flow rate was estimated to be 30%; the reflux rate determined via simulation is subject to errors in the empirical reboiler duty correlation and heat losses from the column and was estimated to be correct to within 25% only. Additional instrumentation (e.g. a more reliable flow meter display unit, accurate measurement of the chilled water flow and a power indicator for the reboiler) would permit a more accurate determination of the reflux rate.

The latent heat of C<sub>4</sub> hydrocarbon is only 30-35% of the latent heat of ethanol. Therefore, a reflux rate of greater than 2.0 L/min is predicted for the expected operating conditions with a reboiler voltage of 180 V. This is acceptable since it permits a reflux ratio of approximately five to be investigated at the proposed feed rate (0.5 L/min), and higher reflux rates and reflux ratios could be investigated with an increased reboiler duty. However, the reflux rates and condenser duties calculated from these tests were significantly lower than anticipated from the condenser performance with water (Section 12.1.6). The relatively high pressures that were observed in the total reflux tests are also apparently inconsistent with the predicted condenser duty. Further tests (e.g. GC analysis of the feed to confirm the concentration of light components) are required to fully determine the source of the discrepancy but the apparent poor thermal performance is mostly due to differences in the physical properties between the test conditions and the expected operating conditions, as described below.

Ethanol has a much lower Prandtl number and a lower thermal conductivity than C<sub>4</sub> hydrocarbon and these differences result in much lower heat transfer rates. The effect is compounded by the low condensation rate of ethanol which reduces the Reynolds' number

and, therefore, produces a lower Nusselt number inside the inner tube. This combination of effects reduces the inner tube heat transfer coefficient by approximately 70% compared with the design conditions. Since the heat transfer rate is controlled by the inner tube heat transfer coefficient and fouling, the influence of the physical properties reduces the overall heat transfer coefficient by 90-95%. Additionally, the flow regime was transitional for these tests and this affects the accuracy of the heat transfer correlation as indicated above (Figure 12.5). A greatly increased condenser duty and, therefore, lower operating pressures are anticipated for the expected operating conditions (i.e. high concentration of  $C_4$ , etc.) due to these factors.

## **CHAPTER THIRTEEN**

### **CONCLUSIONS AND RECOMMENDATIONS**

#### **13.1 Conclusions**

##### **13.1.1 Summary of Research**

##### **13.1.2 Key Findings**

##### **13.1.3 Secondary Findings**

#### **13.2 Recommendations**

### **13.1 CONCLUSIONS AND KEY FINDINGS**

#### **13.1.1 Summary of Research**

Design and control aspects of hybrid reactive distillation for the synthesis of the gasoline oxygenates, ETBE and MTBE, have been studied via steady state and dynamic simulation and experimentation. An accurate and efficient simulation of the reactive distillation process was successfully developed for the steady state case using the equilibrium stage model, and then extended to the dynamic case. These models were used to demonstrate the design and optimisation of various ETBE processes utilising reactive distillation and to investigate the effect of operating variables on the product compositions and yields. A generalised design method for hybrid reactive distillation columns was developed using a combination of residue curve diagrams and simulations.

The steady state and dynamic simulations were also used to investigate multiple steady states (output multiplicity) in reactive distillation and to identify the causes for this phenomenon. Input multiplicity was also investigated with respect to the operation and control of reactive distillation processes. A range of control schemes were implemented via simulation and assessed for their effectiveness and appropriateness for reactive distillation. Open-loop, one-point composition control and two-point composition control were considered.

Simulation results were used to design a reactive distillation pilot plant for the synthesis of ETBE from ethanol and C<sub>4</sub> hydrocarbon from the local oil refinery (BP, Kwinana). The pilot plant was designed to operate at industrially significant pressures and temperatures, and to produce a high ether purity and a high conversion of isobutene to ETBE. It was

constructed and commissioned at Curtin University using novel structured and reactive packings. A fully automatic control system was subsequently installed on the pilot plant in order to implement and test a range of advanced control applications. All aspects of the equipment were tested and found to operate according to design.

### 13.1.2 Key Findings

The following specific conclusions were derived from this research:

- the equilibrium stage model is a satisfactory basis for reactive distillation simulation;
- the response of hybrid columns to changes in operating conditions is often not intuitive and often does not follow the behaviour of non-reactive distillation columns (e.g. the effect of pressure and fractionation changes);
- the dynamic simulation of reactive distillation is possible without using a transformed composition space, provided that the process representation is complete and structured correctly;
- input multiplicity is usually present in hybrid reactive distillation, constraining the pairing of manipulated and controlled variables for linear control systems;
- output multiplicity is sometimes present in hybrid reactive distillation, resulting from at least four fundamental mechanisms (the fourth of which was identified in this work);
- pseudo-multiplicity (described in this work) is often present in reactive distillation but does not necessarily indicate a physically realisable output multiplicity;
- transitions between parallel steady states are possible following a range of common disturbances to the feed composition and rate and various perturbations in manipulated variables;
- output multiplicity compels the use of specific column start-up sequences and effectively excludes the application of many distillation control structures;
- the ether purity and the isobutene conversion can be controlled simultaneously with a simple linear control system, but only if the manipulated and controlled variables are chosen according to specific criteria (outlined here);
- novel packing arrangements were developed to support small catalyst particles within a pilot scale reactive distillation column, and to reduce the cost of non-reactive distillation stages at the laboratory and pilot scales.

### 13.1.3 Secondary Findings

A number of specific conclusions support the key findings:

- the commercial simulation packages, Pro/II™ and SpeedUp™, permitted accurate modelling of reactive distillation operations;
- the SpeedUp™ simulation environment is also effective for the implementation of dynamic simulation models of reactive distillation systems;
- the Pro/II™ simulation environment provided adequate physical property predictions for the successful design of pilot plant equipment (e.g. condenser, reboiler and product cooler) to be used for ETBE synthesis, when combined with conventional design methods;
- the operating pressure of a hybrid reactive distillation column must be optimised to balance the reaction and separation functions of the column;
- increasing fractionation in an hybrid column does not necessarily reduce the energy demand or increase the maximum product purity;
- the production of ETBE is most attractive for hydrocarbon feeds with a relatively low concentration of the reactive component, isobutene;
- a satisfactory design strategy for hybrid columns requires *a priori* study of residue curve diagrams and reactive residue curves, and a rigorous simulation study to produce an optimal design;
- the conversion of MTBE reactive distillation processes to ETBE can sometimes reduce the energy consumption and create equipment redundancies;
- the operation of hybrid columns is considerably more sensitive to the feed composition and the operating conditions compared with non-reactive distillation;
- input multiplicity commonly arises from competing effects that are present in the reactive distillation process;
- uniquely defined input conditions for reactive distillation do not preclude the possibility of more than one steady state operating point;
- singularities in the mass-molar flow relationships and inverse effects from the stage-to-stage energy balances, both known causes of output multiplicity in ideal binary distillation, can also cause output multiplicity in hybrid reactive distillation;
- multiple azeotropes in ternary and pseudo-ternary mixtures, a known cause of output multiplicity in azeotropic distillation, can also cause output multiplicity in hybrid reactive distillation;
- reaction hysteresis can arise from the interactions between the reactive and non-reactive sections of a hybrid reactive distillation column and, where present, can cause output multiplicity;

- many of the reported examples of output multiplicity in reactive distillation are not physically realisable, and only satisfy the criteria for pseudo-multiplicity;
- control schemes which use the distillate rate as the primary manipulated variable are unsuitable for MTBE or ETBE columns due to poor dynamic responsiveness;
- material balance control schemes are unsuitable for MTBE or ETBE columns which exhibit multiple steady states for a constant reboiler duty or reflux rate due to the difficulties in achieving stable inventory control with linear controllers;
- an integrated control strategy can ensure all important operating parameters (i.e. the process performance) remains acceptable following process disturbances and set-point changes, and requires only simple linear controllers to implement;
- the synthesis of ETBE from ethanol and isobutene is feasible in a pilot scale hybrid reactive distillation column using novel packing arrangements for both the reactive and non-reactive column sections.

## 13.2 RECOMMENDATIONS

This research has met the objectives outlined in Chapter 1 and no further work is required. However, there is significant potential to continue the experimental aspects of this research using the reactive distillation pilot plant described in Chapters 11 and 12. In particular, further results could be obtained to demonstrate the viability of ETBE production via reactive distillation and to provide experimental evidence for multiple steady states in this system. Further experimental work would also be useful to test and evaluate the advanced control methods and approaches that were described in Chapters 9 and 10, and to uncover any implementation issues or barriers to industrial application.



## CHAPTER FOURTEEN

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